Modeling the effects of litter stoichiometry and soil mineral N availability on soil organic matter formation using CENTURY-CUE (v1.0)

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Abstract

Microbial decomposition of plant litter is a crucial process for the land carbon (C) cycle, as it directly controls the partitioning of litter-C between CO_2 released to the atmosphere versus the formation of new soil organic matter (SOM). Land surface models used to study the C cycle rarely considered flexibility in the decomposer C use efficiency (CUE_d) defined by the fraction of decomposed litter-C that is retained as SOM (as opposed to be respired). In this study, we adapted a conceptual formulation of CUE_d based on assumption that litter decomposers optimally adjust their CUE_d as a function of litter substrate C to nitrogen (N) stoichiometry to maximize their growth rates. This formulation was incorporated into the widely used CENTURY soil biogeochemical model and evaluated based on data from laboratory litter incubation experiments. Results indicated that the CENTURY model with new CUE_d formulation was able to reproduce differences in respiration rate of litter with contrasting C:N ratios and under different levels of mineral N availability, whereas the default model with fixed CUE_d could not. Using the model with flexible CUE_d, we also illustrated that litter quality affected the long-term SOM formation. Litter with a small C:N ratio tended to form a larger SOM pool than litter with larger C:N ratios, as it could be more efficiently incorporated into SOM by microorganisms. This study provided a simple but effective formulation to quantify the effect of varying litter quality (N content) on SOM formation across temporal scales. Optimality theory appears to be suitable to predict complex processes of litter decomposition into soil C, and to quantify how plant residues and manure can be harnessed to improve soil C sequestration for climate mitigation.

Keywords: microbial carbon use efficiency, litter decomposition, litter stoichiometry, soil organic matter, litter decay model, nitrogen

1 Introduction

Plant litter decomposition plays a key role in global carbon (C) cycle, thus needs to be well represented in land surface models. The decomposition and transformation processes of plant litter control the formation of soil organic matter (SOM) (Prescott, 2010; Schmidt *et al.*, 2011; Walela *et al.*, 2014; Cotrufo *et al.*, 2015) and associate immobilization and mineralization of essential plant nutrients (Moorhead and Sinsabaugh, 2006; Parton *et al.*, 2007; Manzoni *et al.*, 2008; Manzoni and Porporato, 2009). Hence, a reliable litter decay model is necessary for estimating soil C balance and turnover of ecosystem C (Allison, 2012; Bonan *et al.*, 2013; Wieder *et al.*, 2013; Campbell and Paustian, 2015). In particular, a realistic representation of litter decomposition in land surface models is helpful to decrease the uncertainties in predicted effects of climate change and anthropogenic management on ecosystems (Gholz *et al.*, 2000; Campbell and Paustian, 2015; Luo *et al.*, 2016). As litter decomposition is a very complex process determined by climate (e.g. temperature and moisture), litter quality (e.g. nitrogen (N) concentration), soil nutrients and the physiological characteristics of microorganisms (Lekkerkerk *et al.*, 1990; Prescott, 2010; Manzoni *et al.*, 2012; Frey *et al.*, 2013; Sinsabaugh *et al.*, 2013; García-Palacios *et al.*, 2016), there remain large uncertainties in existing litter decay models (Zhang *et al.*, 2008; Bonan *et al.*, 2013; Campbell and Paustian, 2015). Many litter decay models, especially those incorporated in global land surface models, have ignored stoichiometric constraints to microbial processes (Bonan *et al.*, 2013; Cotrufo *et al.*, 2013; Wieder *et al.*, 2013; Wieder *et al.*, 2014).

Microbial carbon use efficiency (CUE),defined as the ratio of microbial biomass production to material uptake from substrates (Lekkerkerk *et al.*, 1990; Manzoni *et al*., 2012), is an important parameter constraining litter decay, but it has rarely been represented as a flexible quantity in land surface models. During litter decomposition, only a part of the decomposed litter-C is being transferred into SOM, while the remaining C is being released as CO_2 to the atmosphere by microbial respiration (Campbell and Paustian, 2015; Cotrufo *et al*., 2015). While CUE is a

74   physiological property of each decomposer community, it also determines the

75   ecosystem-level efficiency at which litter C is transferred into SOM a step further from

76   simple microbial incorporation. We denote this efficiency as carbon use efficiency of

77   litter decomposition (CUE_d). With higher CUE_d, more plant-produced litter is

78   transformed biologically into SOM, and soil C storage can reach higher values (Six *et*

79   *al.*, 2006; Sinsabaugh *et al.*, 2013). In most existing soil biogeochemical models,

80   CUE_d is assumed to be same as microbial CUE and considered as a fixed parameter.

81   The Verberne model (Verberne *et al.*, 1990) assumes for instance $CUE_d \approx 0.25$. In the

82   Yasso model (Liski *et al.*, 2005), the CUE_d is set to 0.2. The CENTURY model sets

83   the CUE_d for decomposition of surface and belowground metabolic litter to 0.55 and

84   0.45, respectively (Parton *et al.*, 1988). In Daisy (Hansen *et al.*, 1991), NCSOIL

85   (Molina *et al.*, 1983) and ICBM (Kätterer and Andrén, 2001), $CUE_d = 0.6$ for the

86   labile litter pools and takes a lower value for recalcitrant substrates. Only a few

87   models account for variable CUE, letting it vary in response to substrate

88   stoichiometry (Schimel and Weintraub, 2003) or temperature (Allison *et al.*, 2010).

89   The increasing evidence for a variable microbial CUE leads to a conceptual

90   CUE model which can explain trends in CUE of microorganisms along stoichiometric

91   gradients (Manzoni *et al.*, 2017). The values of CUE_d used in existing litter decay

92   models are mostly derived from CUE obtained in laboratory studies on microbial

93   physiology or limited observations in certain ecosystems, thus show large variations

94   without a dynamic link to environmental conditions (Parton *et al.*, 1988; Verberne *et*

95   *al.*, 1990; Hansen *et al.*, 1991; Liski *et al.*, 2005; Manzoni *et al.*, 2012). Recent studies

96   (Manzoni *et al.*, 2008, 2012) suggested that the microbial CUE in terrestrial

97   ecosystems ranges from less than 0.1 for wood decomposers to about 0.5 for

98   decomposition of N-rich and high-quality litter. To explain those differences, Manzoni

99   *et al*. (2017) proposed a conceptual model of microbial CUE based on the assumption

100   that decomposers adapt their metabolism (and hence CUE) to maximize their growth

101   rate. This model based on optimality theory links CUE to substrate and decomposers

102   stoichiometry, where the optimal CUE decreases with increasing substrate

103   C-to-nutrient ratio, and increases with soil nutrient availability. The predictions of this

theoretical model have been verified by empirical evidence from CUE estimates for different microorganisms in both aquatic and terrestrial ecosystems (Manzoni *et al.*, 2017).

Besides variable CUE_d, many previous studies have also indicated the necessity for litter decomposition models to consider soil mineral N availability as a driver of litter decomposition rates, in particular under low N availability (Wieder *et al.*, 2015; Luo *et al.*, 2016; Averill and Waring, 2018). Microbial biomass is nearly homeostatic (Cleveland and Liptzin, 2007; Franklin *et al.*, 2011; Allison, 2012). When the supply of N from substrates is lower than the demand of microbes to fulfill their specific stoichiometric C:N ratio, microbes will utilize mineral N (immobilization) (Manzoni *et al.*, 2012). Thus, low availability of mineral N can limit microbial activity, and in turn litter decay rate (Manzoni and Porporato 2009; Fujita *et al.*, 2014). Although there are fertilization experiments reporting insignificant or even negative impacts of added N on litter decay rate (Fog, 1988; Hobbie and Vitousek, 2000; Finn *et al.*, 2015), many incubation experiments showed a significant decrease of litter decomposition rate with declining mineral N availability (Recous *et al.*, 1995; Hobbie and Vitousek, 2000; Guenet *et al.*, 2010). Moreover, recent modeling studies have indicated that including the limiting effect of low mineral N on decomposition improved predictions of C and N fluxes (Bonan *et al.*, 2013; Fujita *et al.*, 2014). Therefore, soil mineral N can alter litter C flux by affecting both the litter decay rate and the partition of decayed litter-C (via flexible CUE_d).

Some detailed microbial decomposition models actually have included variable microbial CUE and the limitation of low mineral N availability on litter decay rate (Ingwersen *et al.*, 2008; Pagel *et al.*, 2013; Campbell *et al.*, 2016; Huang *et al.*, 2018); however, the parameterization and evaluation of these models pose significant challenges due to their complexity and limited verification data (Wieder *et al.*, 2014; Campbell and Paustian, 2015). There is still scope for implementing the effects of litter stoichiometry and soil mineral N availability on litter decomposition in litter decay models with more generalizable structure. In particular, it is important to test the role of these effects in models that have already been incorporated into land

surface model for long-term and large-scale applications (e.g. CENTURY, Parton *et al.*, 1988). In this study, we incorporated flexible CUE_d based on substrate C:N ratios and mineral N limitations into a soil biogeochemical model based on the CENTURY equations to simulate the decomposition and transfer processes of litter-C. The study was organized as follows. First, the new model was calibrated and tested against data from laboratory litter incubation experiments for its ability to capture the effect of variable litter quality and soil mineral N on litter respiration rates (short-term simulations). Second, the model parameterized assuming flexible CUE_d and mineral N limitations was used to explore the consequences of such stoichiometric constraints on the production of soil organic carbon (SOC) (long-term simulations). With these two modeling analyses, we aimed at linking stoichiometric constraints acting on short-term (months to years) decomposition dynamics to their consequences on SOC accumulation occurring at decadal to centennial time scales.

2 Materials and methods

2.1 The CENTURY decomposition model

The basis of the litter decay model used in this study is the CENTURY model (Fig. 1), a first-order decay model that describes decomposition as a function of substrate availability and quality, clay content, soil moisture and soil temperature (Parton *et al.*, 1988). Most land surface models (e.g. Kucharik *et al.*, 2000; Sitch *et al.*, 2003; Krinner *et al.*, 2005) adopted a similar structure to simulate the litter and soil biogeochemical processes. Dead organic matter in CENTURY is separated into structural and metabolic litter and three SOM pools (active, slow, passive) with different turnover times. There is no explicit representation of microbial biomass in CENTURY, instead the biomass of microbes is assumed to be in equilibrium with labile SOM and thus implicitly included in the active SOM pool. When C is being decomposed, a fraction of the decomposed C is respired to the atmosphere and the remaining fraction (CUE_d conceptually equal to microbial CUE) enters the acceptor SOM pool. Three of such fractions are defined to characterize the transfer of C from

163   litter to SOM: CUE_{ma} for transfer of the metabolic litter to the active SOM pool, and

164   CUE_{sa} and CUE_{ss} for transfer of structural litter to active and slow SOM pools,

165   respectively (Fig. 1).These fractions are set to be time invariant in the original version

166   of CENTURY, so that a fixed fraction of decomposed C is retained in the acceptor

167   pool regardless of environmental conditions and changes in the quality of the donor

168   pool. The N flows in CENTURY follow the C flows and are equal to the product of C

169   flow by the N:C ratio of the acceptor SOM pool. N mineralization is defined as the

170   difference between N obtained from the donor pools and N stoichiometric demand of

171   the acceptor pool (Parton et al., 1988; Metherell et al., 1993). In this way, net N

172   mineralization occurs when the donor pool has low C:N ratio, but N is immobilized

173   (taken up by microbes) when the donor pool has high C:N ratio.

174

175   2.2 Optimal CUE

176   To quantify how microbial CUE varies along gradients of nutrient

177   availability, it can be hypothesized that microorganisms maximize their growth rate,

178   and hence their ecological competitiveness, by adapting resource (C and nutrients) use

179   efficiencies. This follows the growth maximization hypothesis (Mooshammer *et al*.,

180   2014; Manzoni *et al*., 2017). Based on this hypothesis, Manzoni *et al*. (2017)

181   formulated a theoretical model expressing microbial CUE as a function of the

182   stoichiometric difference between decomposers and their substrate. The CUE for

183   which growth rate is maximized is the optimal CUE (CUE_{opt}) given by:

184    $$CUE_{opt} = CUE_{max} \times \min\left[1, \frac{CN_D}{CUE_{max}} \times \left(\frac{1}{CN_S} + \frac{I_N}{U_0}\right)\right] \qquad (1)$$

185   where CUE_{max} is the maximum microbial CUE (dimensionless) when growth is

186   limited by C from the organic substrate. CN_D and CN_S are the C:N ratio (in mass,

187   dimensionless) of decomposer and their substrate, respectively. Although Manzoni *et*

188   *al*. (2017) indicated that mineral phosphorus (P) could also affect optimal CUE we

189   only considered N as a limiting nutrient. I_N (g N kg^{-1} soil) is the maximum rate at

190   which mineral N can be taken up by microbes, and U_0 (g C kg^{-1} soil) is the C-limited

191   uptake rate (corresponding to the decomposition rate at optimal mineral N

192 concentration). When litter C:N is low or soil mineral N is in excess, the second term

193 in the minimum function (Eq.(1)) is higher than one, and $CUE_{opt} = CUE_{max}$ (C limited

194 conditions, as in nutrient-rich litter). In contrast, when mineral N is scarce, CUE_{opt}

195 decreases with increasing substrate C:N ratio (N limited conditions, N-poor litter).

196 Lack of N in the organic substrates can be compensated by mineral N being

197 immobilized by microorganisms from the soil solution. Immobilization meets the

198 nutrient demands as long as it is lower than the maximum supply rate I_N, at which

199 point microbial CUE starts being down regulated. Thus, for any given C:N ratio in the

200 substrate, CUE_{opt} increases with inorganic N concentration in the soil solution until

201 CUE_{max} is reached. It should also be noted that Eq. (1) is interpreted at the microbial

202 community scale, not for individual organisms.

203

204 2.3 Adaption of the optimal CUE model in the CENTURY model

205   CUE of decomposition (CUE_d) is also assumed to be equivalent to microbial

206 CUE in this study. Then we followed the theory from Manzoni *et al*. (2017) (Eq. (1))

207 to parameterize CUE_d during litter decomposition into CENTURY (Fig.1). Due to the

208 implicit representation of microbial growth in CENTURY, we replaced the original

209 optimality CUE model (Eq. (1)) by a simpler equation that involves the C:N ratios of

210 the donor and acceptor pools, rather than microbial C:N ratios:

211 $$CUE_{opt} = CUE_{max} \times \min\left[1, \left(\frac{CN_{lit}}{CN_{SOM}}\right)^a\right] \qquad (2)$$

212 where CN_{lit} and CN_{SOM} are the C:N ratio (dimensionless) of litter (metabolic or

213 structural) and SOM pools (active, slow or passive), respectively. The C:N ratio of

214 SOM (around 9:1 on a mass basis in CENTURY) is representative of the decomposer

215 biomass, its value being between the average C:N ratio of soil microbial communities

216 including fungi and bacteria (7.4:1 in Cleveland and Liptzin, 2007) and the C:N ratio

217 of soil fungi (13.4:1 in Zhang and Elser, 2017), which are probably largely

218 responsible for fresh litter decomposition. CUE_{max} (dimensionless) is the maximum

219 CUE_d achieved when nutrients are not limiting, and it is set to 0.8 based on a

220 synthesis of observed CUE of soil microbes (Manzoni *et al*., 2012). The exponent *a* (g

221 N kg^{-1} soil) captures the effect of mineral N uptake by microbes on CUE_d. Because

222 CUE_d is expected to increase with mineral N availability (Eq. (1)), a is assumed to be

223 a linear function of the mineral N concentration (N_{min}, g N kg^{-1} soil):

224 $$a = m_1 \times (N_{min} - n_1)$$ (3)

225 where m_1 (kg g^{-1} N) and n_1 (g N kg^{-1} soil) are two coefficients that need to be

226 calibrated. Eqs. (2) and (3) modulate the decrease in CUE_d with decreasing litter

227 quality when mineral N availability changes– the exponent a increases with

228 increasing mineral N availability, causing an increase in CUE_d at any given litter C:N

229 ratio. Hence, increasing a mimics an increase in I_N in Eq. (1). Fig. 2a illustrates how

230 CUE_d from Eq. (2) varies as a function of mineral N concentration, for different

231 values of litter C:N.

232   Eqs. (2) and (3) were implemented in CENTURY to modify the originally

233 fixed CUE_d (Fig. 1). With this change, the fractions of C from litter that remain in

234 SOM are mediated by stoichiometric constraints and mineral N availability, at the

235 expense of additional parameters to fit. The CUE_d for C transfers between SOC pools

236 (active, slow and passive) are not modified.

237

238 2.4 Constraint of soil nutrient availability on litter decomposition rate

239   CENTURY is a first-order decay model in which decomposition rates of

240 metabolic and structural litter are modulated by scaling factors of soil temperature

241 ($f(tem)$) and moisture ($f(water)$) (Parton *et al.*, 1988). Here, we introduced an

242 additional mineral N scaling factor ($f(N_{min})$, 0–1, dimensionless) to account for the

243 limitation imposed by low mineral N availability on litter decay rate ($D(C_{lit})$).

244 $$D(C_{lit}) = C_{lit} \times k \times f(tem) \times f(water) \times f(N_{min})$$ (4)

245 where C_{lit} is the C (g C kg^{-1} soil) in litter pool (metabolic or structural) and k is the

246 potential maximum turnover rate (day^{-1}) at optimal soil temperature, moisture and

247 nutrient conditions.

248   In this study, we assumed that the scaling factor of mineral N increases

249 linearly with increasing soil mineral N concentration (N_{min}, Eq. (5)) below a threshold

250 value of $1/m_2$ g N kg^{-1} soil, where m_2 is a positive coefficient which needs to be

251 calibrated (Fig.2b). The inhibition effect of mineral N only occurs in case of

252 immobilization ($1/CN_{lit} < CUE_{opt}/CN_{SOM}$). The specific function $f(N_{min})$ can be

253 expressed as:

$$254 \qquad f(N_{min}) = \begin{cases} \min(1, m_2 \times N_{min}) , & \frac{CUE_{opt}}{CN_{SOM}} - \frac{1}{CN_{lit}} > 0 \\ 1 & , & \frac{CUE_{opt}}{CN_{SOM}} - \frac{1}{CN_{lit}} \leq 0 \end{cases} \qquad (5)$$

255   Existing studies have adopted approaches that differ from our definition to

256 explicitly represent the N inhibition effects on microbial processes (Manzoni and

257 Porporato, 2009; Bonan *et al.*, 2013; Fujita *et al.*, 2014; Averill and Waring, 2018). In

258 these previous studies, $f(N_{min})$ was assumed equal to the ratio between immobilized

259 mineral N and the N deficit for maintaining a stable C:N of decomposer biomass or

260 other receiver pools. Using the notation of Section 2, this definition of $f(N_{min})$ can be

261 expressed as:

$$262 \qquad f(N_{min}) = \begin{cases} \min\left(1, \frac{m_3 \times N_{min}}{U_0 \times \left(\frac{CUE_{opt}}{CN_{SOM}} - \frac{1}{CN_{lit}}\right)}\right) , & \frac{CUE_{opt}}{CN_{SOM}} - \frac{1}{CN_{lit}} > 0 \\ 1 & , & \frac{CUE_{opt}}{CN_{SOM}} - \frac{1}{CN_{lit}} \leq 0 \end{cases} \qquad (6)$$

263 where m_3 is a coefficient that needs to be optimized. U_0 (g C kg^{-1} soil day^{-1}) is the C

264 uptake rate (equivalent to the litter decomposition rate in absence of leaching) when

265 soil mineral N is fully adequate for litter decay (i.e. $f(N_{min}) = 1$), and can be calculated

266 from Eq. (7) as:

$$267 \qquad U_0 = C_{lit} \times k \times f(tem) \times f(water) \qquad (7)$$

268 In this study, we also tested this formulation in the CENTURY-based model, in

269 addition to the Eq. (5) (see model M4 in Table A3).

270

271 2.5 Model parameterization and validation

272   To determine the respective impacts of including flexible CUE_d and N

273 availability constraining decay rates, we built four conceptual litter decay models

274 (Table 1). Model M0 corresponds to the default CENTURY parameterization of a

275 fixed CUE_d and no constraints of N availability on litter decay rates ($f(N_{min}) = 1$).

276 Model M1accounts for flexibility in CUE from Eq. (2) and N constraints on decay

277   rates by Eq. (5). Model M2 has flexible CUE_d but no N constraints on decay rates

278   ($f(N_{min})= 1$). Model M3 has N constraints on decay rates but a fixed CUE_d (Table 1).

279   All of these four models are run at a daily time step. Finally, model M4 also accounts

280   for flexibility in CUE and N constraints on decays (Table A3), but it uses Eq. (6) to

281   represent the N constraints on decays rate rather than Eq. (2). Results from model M4

282   are presented in the main text, but only shown in the Appendix. This range of models

283   allows identifying which mechanisms are at play during decomposition – flexible

284   CUE_d only (M3), mineral N limitation only (M2), both mechanisms (M1, M4), or

285   none (M0).

286   For calibrating model parameters and evaluation of their results, we collected

287   data of laboratory litter incubation experiments from Recous *et al*. (1995) (5

288   experiments) and Guenet *et al*. (2010) (9 experiments, Table A2). The incubation

289   experiments of Recous *et al*. (1995) and Guenet *et al*. (2010) continued 80 and 124

290   days, respectively. Recous *et al*. (1995) used corn residues (C:N = 130) and Guenet *et*

291   *al*. (2010) used wheat straw (C:N = 44) in their incubation experiments. The C:N

292   ratios of those corn residue and wheat straw span the range of litter C:N ratios among

293   different ecosystems (Harmon *et al*., 2009; Brovkin *et al*., 2012; Manzoni *et al*., 2010).

294   In the incubation experiments, plant litter was firstly cut into fine fragments before it

295   was mixed with mineral soil. Soil temperature and moisture condition were kept

296   constant during the experiment. Respired C from the incubated litter and SOC, as well

297   as the soil mineral N concentrations were measured continuously across the

298   incubation period. To distinguish the litter- and SOC-derived CO_2 flux, Guenet *et al*.

299   (2010) used straw from wheat grown under ^{13}C labeled CO_2 and they are therefore

300   able to track the CO_2 coming from litter and the CO_2 coming from soil. In the

301   experiments by Recous et al. (1995), litter-derived CO_2 flux is calculated as the

302   difference in CO_2 flux between the incubation samples with both soil and litter, and

303   the control samples without added litter. More detailed information about the

304   incubation experiments of Recous *et al*. (1995) and Guenet *et al*. (2010) can be found

305   in Table A2.

306   The initial C storage and C:N ratios of litter and SOM pool, as well as soil

307 temperature and moisture condition for decomposition in all of the five versions of the

308 model (M0-M4) were set based on observations (Table A2). Plant litter was firstly

309 separated into metabolic and structural litter pools based on its lignin to C ratio (LC_{lit},

310 dimensionless). The fraction of metabolic litter-C (f_m, 0-1, dimensionless) is

311 calculated by:

312 $$f_m = f_{max} - m_4 \times LC_{lit} \tag{8}$$

313 where m_4 is a coefficient to be calibrated; f_{max}=0.85 is the maximum fraction of

314 metabolic litter (i.e., the default value in CENTURY; Parton *et al*., 1988). The

315 fraction of structural litter-C is thus 1- f_m. The C:N ratios of both metabolic and

316 structural pools are assumed to be equal to the C:N ratio of litter input.

317   In M1 and M3 models, the observed mineral N concentrations across the

318 incubation period were used to calculate the daily N inhibition effect (Eq. (5)). The

319 observed cumulative respired litter-C (g C kg^{-1} soil) measured in the incubation

320 experiments was used to calibrate the model parameter values. Moreover, to quantify

321 the simulated CO_2 flux derived from the litter, we also performed a set of control

322 simulations with only SOM (initial litter pools were set to 0 g kg^{-1} soil) using the four

323 model versions. The simulated litter-derived CO_2 flux is calculated as the difference

324 in CO_2 flux between the simulation with both litter and SOM inputs and the

325 simulation with only SOM input.

326   Parameter calibration was performed for each model with the shuffled

327 complex evolution (SCE) algorithm developed by Duan *et al*., (1993). The SCE

328 algorithm relies on a synthesis of four concepts that have proved successful for global

329 optimization: combination of probabilistic and deterministic approaches; clustering;

330 systematic evolution of a complex of points spanning the space in the direction of

331 global improvement and competitive evolution(Duan *et al.*, 1993). A more detailed

332 description of this SCE optimization method can be found in Duan *et al*. (1993, 1994).

333 In this study, the RMSE (root mean square error, Eq.(9)) between simulated and

334 measured cumulative respired litter-C (%) on all observation days (Table A2) of each

335 incubation experiment was used as the objective function, and the parameters

336 minimizing RMSE between simulated and observed cumulative respired litter-C were

337   regarded as optimal parameter values.

338    $$RMSE = \sqrt{\left(\frac{\sum_{i=1}^{n}(Sim_i - Obs_i)^2}{n}\right)} \qquad (9)$$

339   where n is the number of observation days, Sim_i and Obs_i (%) are the simulated

340   and observed percent of cumulative litter-C flux on day i, respectively.

341   We used leave-one-out cross-validation (Kearns and Ron, 1997; Tramontana

342   *et al.*, 2016) to evaluate each of the four models (i.e. M0-M3), a cross validation

343   method used when data is scarce. The number of cross-validations corresponds to the

344   number of incubation experiments (14). Each time, one of the 14 incubation

345   experiments was left out as the validation sample, and the remaining 13 experiments

346   were used to train model parameters. In addition to RMSE, we also adopted the

347   Akaike Information Criterion (AIC, Bozdogan, 1987, Eq. (10)) to determine the

348   relative quality of the four version models on estimating cumulative respired litter-C.

349    $$AIC = n \times ln\left(\frac{\sum_{i=1}^{n}(Sim_i - Obs_i)^2}{n}\right) + 2n_p \qquad (10)$$

350   where n_p is the number of model parameters. The evaluation of AIC is important here

351   because depending on the model version, different numbers of parameters have to be

352   determined (Table 1), requiring us to weigh both model accuracy and robustness.

353   Note that the turnover times of SOM pools (active, slow and passive) used in

354   this study are obtained from the ORCHIDEE-MICT (v8.4.1, Guimberteau *et al*.,

355   2018). The turnover times of litter pools (metabolic and structural), as well as the

356   coefficient m_4 in Eq. (8) were optimized against the observed cumulative respired

357   litter-C from all of the 14 incubation experiments using the M0 and M1 models (Table

358   A3). A previous study has shown that litter decomposability is negatively correlated to

359   its physical size (for example, Tuomi *et al*., 2011). Therefore, the turnover times of

360   the fine litter fragments used in the incubation experiments of Recous *et al*. (1995)

361   and Guenet *et al*. (2010) are expected to be shorter than the values set in

362   ORCHIDEE-MICT, which are representative of the turnover times of natural plant

363   residues. In addition, the mixing of soil and litter particle in the incubation experiment

364   likely enhances decomposition as spatial disconnection of decomposer and substrate,

365   which can occur under natural soil conditions (Barnes *et al*., 2012; Hewins *et al*.,

366 2013), is prevented. The calibrated turnover times of the metabolic and structural

367 pools and the value of m_4 in Eq. (8) are 3.5 and 30 days and 0.5, respectively.

368

369 2.6 Impacts of litter stoichiometry and mineral N availability on SOM accumulation

370 We used the model M1, with flexible CUE_d and decomposition rate function

371 of available N to study the impacts of litter stoichiometry (C:N ratio) and soil mineral

372 N availability on the formation and accumulation of SOM. In total, 24 idealized

373 simulation experiments with different values of litter C:N ratios and soil mineral N

374 availabilities were conducted (Table A4). The assumed litter C:N ratios (CN_{lit}) of 10,

375 15, 30, 60, 120 and 200 span the variation among most natural substrates and soil

376 amendments from organic matter input in agriculture (Harmon et al., 2009; Brovkin *et*

377 *al*., 2012; Manzoni *et al*., 2010). The assumed range of mineral N availability (N_{min})

378 of 0.001, 0.005, 0.01 and 0.05 g N kg^{-1} soil span the observed concentrations of soil

379 mineral N in major terrestrial ecosystems (Metherall *et al.*, 1993).

380 In each simulation experiment, model M1 was run for 5000 years to bring the

381 litter and SOM pools in equilibrium with the prescribed litter input flux. The daily

382 input rate of plant litter was set to 0.006 g C kg^{-1} soil day^{-1}, and the initial C stock of

383 litter and SOM pools were all set to be 0 g C kg^{-1} soil. During the simulation, soil

384 temperature and soil water content were assumed to be 25 °C and 60% of water

385 holding capacity, respectively. We emphasized that our goal with this simplified

386 scenario was to single out the effects of stoichiometric constraints, not to simulate the

387 effects of a realistic climatic regime. Parameter values for M1 (with $m_1 = 0.54$, $n_1 =$

388 0.50 and $m_2 = 296.8$) used here were optimized based on all of the 14 incubation

389 experiments from Recous *et al*. (1995) and Guenet *et al*. (2010) (see above). More

390 detailed information about the specific settings of our simulation experiments can be

391 found in Table A4.

392

393 **3 Results**

394 3.1 Evaluation of different models

395   Results of leave-one-out cross-validation suggest that model M1 provides

396 more accurate prediction of cumulative respired litter-C than other models (Fig. 3).

397 The differences between simulated and observed cumulative respired litter-C from

398 M1 are mostly less than 6% for over 93% of the data (Fig. A1b). The average RMSE

399 of predicted cumulative respired litter-C from M1 (3.0%) is lower than that of model

400 M0 (4.1%). Models M2 and M3 have slightly lower RMSE values than M0 (3.7% and

401 3.8%, respectively) but perform worse than M1 (Fig.4). However, the average AIC of

402 all the models are comparable, suggesting that models with more fitted parameters do

403 not over-fit the observations (Fig. 4).

404   Model M1 captures the differences in respiration rates due to different C:N

405 ratios of substrate and varying levels of mineral N availability across the 14

406 incubation experiments (Fig.5). While model M3 can reproduce the observed effect of

407 soil mineral N availability on litter respirations rates (Fig.5d), it underestimates the

408 cumulative respired CO_2 from low quality litter ($CN_{lit} = 130$) at high mineral N

409 concentrations (> 0.04 g N kg^{-1} soil). Models M0 and M2 cannot represent the effects

410 of soil mineral N on litter respiration rate (Figs.5a, c), and their predictions are more

411 biased from the observed values compared to M1. The Model M4, which uses the

412 alternative formulation for N constraints on litter decay (Eq. (6)), reproduces the

413 different respiration rates of substrates with contrasting C:N ratios and at different

414 levels of mineral N availability (Fig. A2), but with a slightly higher average RMSE of

415 cumulative respired litter-C than model M1.

416   The predicted CUE_d and the limitation effects of soil mineral N availability

417 on litter decay rate ($f(N_{min})$ function Eq. (5)) are different among the four tested

418 models (Fig. A3). In models M0 and M3, which used a fixed CUE_d, the fitted values

419 of CUE_d calculated with optimized parameters during the incubation period are about

420 0.57 and 0.54, respectively (Figs. A3a, d). In models M1 and M2, the CUE_d varies

421 with the C:N ratios of plant litter, and is only slightly affected by soil mineral N

422 concentrations (Figs. A3b, c). For very low quality litter with a C:N ratio of 130, the

423 CUE_d in models M1 and M2 are 0.40 and 0.44, respectively, which are lower than for

424 better quality litter with C:N ratio of 44 (approximately 0.55 and 0.56 in M1 and M2,

425 respectively). Models M0 and M2 do not include the N inhibition effects on litter

426 decay rate, thus the $f(N_{min})$ in these two models is always 1 (Figs. A3e, g). In M1 and

427 M3, the N inhibition effect changes with both the litter C:N ratio and the mineral N

428 availability (Figs. A3f, h).

429 CUE_d from Eq. (2) calibrated with the data of the two incubation

430 experiments, decreases with increasing CN_{lit}/CN_{SOM} (Fig. 6). The average CUE_d value

431 is larger than the average of data compiled for microbial CUE of litter decomposition

432 in terrestrial ecosystems by Manzoni *et al.* (2017). This is shown by the gray circles in

433 Fig. 6. Our optimized values of CUE_d for a given C:N ratio are more comparable with

434 microbial CUE observed in incubations of soil mixed with litter (Gilmour and

435 Gilmour, 1985; Devêvre and Horwáth, 2000; Thiet *et al.*,2006), shown as black

436 squares in Fig. 6.

437

438 3.2 The effect of litter quality *vs* quantity on equilibrium SOM stocks

439 Model M1 predicts that the size of the SOM pool at equilibrium is mainly

440 determined by litter stoichiometry, with a minor effect of soil mineral N (Fig. 7). The

441 lower C:N ratio of litter is, the higher equilibrium SOC stock. For litter with a specific

442 C:N ratio, high soil mineral N concentration (e.g. above 0.05 g N kg^{-1} soil) generally

443 produces a slightly larger equilibrium SOC stock than a low mineral N concentration

444 (Fig. 7). Further analysis suggests that the SOC at equilibrium increases with

445 decreasing litter C:N because the SOC pool is positively related to the CUE_d; however

446 the limitation of soil mineral N on litter decomposition rate almost shows no impact

447 on SOC (Fig. A4).

448

4 Discussion

450 We hypothesized that stoichiometric constraints (flexible CUE_d or inhibition

451 of decomposition under N limited conditions) played a role in shaping the trajectory

452 of litter decomposition, with potential consequences on predicted SOC stocks. Our

453 results suggest that flexible CUE_d and inhibition effects of soil mineral N on litter

decay rate improve prediction of litter decomposition when using a modified version

of CENTURY model (denoted as M1). Evaluation of the model M1 using data from

incubation experiments indicate that this modified model captures the effects of both

variable litter quality (stoichiometry) and mineral N availability on respiration rates

(Fig. 5), without strongly inflating the complexity of CENTURY (Table 1). As the

stoichiometric constraints are implemented in the generalizable and widely used

structure of CENTURY and require only three parameters to be calibrated, they can

also be easily implemented into land surface models for large spatial scale

applications.

Accurately representing N control of microbial processes during litter

decomposition has been suggested to be important for modeling the connection

between the litter inputs, CUE_d, and soil C dynamics (Gerber *et al*., 2010; Manzoni *et*

al., 2012; Cotrufo *et al.*, 2013; Sinsabaugh *et al.*, 2013). In model M1, soil mineral N

affects the litter-C flux via two mutually different pathways: (1) mineral N availability

affects the litter decay rate and (2) flexible CUE_d determining the partition of

decomposed C into SOC products and respired CO_2 (Fig. 1). Therefore, an increase in

soil mineral N concentration enhances litter decay rates, which alone will increase the

flux of litter-derived CO_2 (Eq. (5) and Fig. A5). However, as higher N concentration

also results in a higher CUE_d (Eq. (2)), more C is transferred to SOC and less C is

respired. In this way, SOC is predicted to accumulate with increasing mineral N

availability when using model M1 (Fig. 7). In addition, the model M4, which is

comparable to model M1 but uses an alternative formulation for N effects on the

decomposition rate (Eq. (6)), performed slightly worse than model M1 (Fig. A2).

Arguably, Eq. (6) represents the underlying mechanisms of N inhibition effects

(Manzoni *et al.*, 2009; Bonan *et al.*, 2013; Fujita *et al.*, 2014; Averill and Waring,

2018) better than Eq. (5) and due to the minor differences in RMSE and AIC (Figure

A2b) between these formulations it can serve as an alternative to M1.

Our results indicate that the observed diversity of responses of litter

respiration rate to mineral N additions (Hobbie and Vitousek, 2000; Guenet *et al.*,

2010; Janssens *et al.*, 2010) is likely due to the combined effects of changes in litter

484   decay rate and CUE_d (Fig. A5). Thus, N addition effects can differ among fertilization

485   experiments if litter quality and background N availability vary. In addition to altering

486   litter decay rate and CUE_d, mineral N addition can induce abiotic formation of

487   compounds that resist microbial attack, inhibit oxidative enzymes involved in lignin

488   degradation, stimulate microbial biomass production early in decomposition, or lead

489   to the accumulation of microbial residues that are resistant to decay (Fog, 1988;

490   Hobbie, 2015). All these effects might decrease litter respiration rate by inhibiting the

491   decomposition process, but have not been considered in our current model.

492   This study provides insights on processes leading to increased SOM

493   sequestration. Enhancing the efficiency at which plant residuals are transformed into

494   stable SOM has been suggested as an effective strategy to sequester C in soil (Prescott,

495   2010; Cotrufo *et al.*, 2013). Simulation results from our model suggest a positive

496   linear relationship between equilibrium SOC stock and CUE of decomposed litter

497   (Fig. A4), in line with the earlier findings with a similar model (for example Frey *et al*.

498   2013). In fact, with linear models such as CENTURY it can be shown that the steady

499   state SOC scales linearly with CUE, different from nonlinear models predicting that

500   higher CUE can trigger SOC loss (Allison *et al*., 2010). Our model goes beyond

501   earlier attempts (Bonan *et al.*, 2013; Fujita *et al.*, 2014; Averill and Waring, 2018) by

502   adapting the optimal metabolic regulation hypothesis of Manzoni *et al*. (2017) to link

503   CUE, litter quality and SOM formation in a process-oriented way.

504   The importance of litter quality for SOM formation as found here is in line

505   with recent experiments (Bahri *et al*., 2008; Rubino *et al*., 2010; Walela *et al*., 2014)

506   and modeling studies (Grandy and Neff, 2008; Cotrufo *et al.*, 2013). SOM is mainly

507   formed though the partial decomposition of plant debris by microorganisms (Paul,

508   2007; Knicker, 2011; Cotrufo *et al.*, 2013). The conceptual model developed by

509   Cotrufo *et al*. (2013) suggested that although labile litter was decomposed faster than

510   recalcitrant litter, a higher fraction of this labile litter-C would be incorporated into

511   microbial biomass and subsequently incorporated into SOM pool (corresponding to a

512   higher CUE_d). Therefore, labile litter inputs tend to form a larger SOM pool than the

513   poor-quality (high C:N ratio) litter that is generally used by microbes at lower

514   efficiency. Our simulations of decomposition process of plant litter with different C:N

515   ratios also suggest that litter of good quality (with low C:N ratio) can induce a larger

516   SOM pool than the poor-quality litter (Fig. 7). CUE_d plays a more important role than

517   the inhibition effect of low mineral N concentration in determining the size of the

518   stable SOM pool (Fig. A4).

519   The predictions from Cotrufo *et al*. (2013) and this study contrasts with the

520   conventional hypothesis whereby the poor-quality litter with low decay rate and small

521   CUE_d are preferential to be accumulated in SOM (Berg and Mcclaugherty, 2008;

522   Walela *et al.*, 2014).This view of SOM stabilization, however, seems to apply to

523   N-limited systems with high C:N litter and where microbial remains are recalcitrant to

524   decomposition (e.g., boreal forests) – in these systems SOC does accumulate despite

525   its low quality (Kyaschenko et al. 2017). Moreover, one could argue that higher CUE_d

526   implies larger microbial biomass, allowing faster decomposition (Allison et al., 2010).

527   These feedbacks between microbial biomass and decomposition rate were not

528   implemented in the current model, but could offer additional flexibility – again at the

529   expense of more difficult model parameterization.

530   The CUE_d formulation from Eq. (2) with parameters calibrated from the two

531   sets of incubation experiments might underestimate the impacts of litter quality on

532   microbial CUE under natural conditions, in particular in case of SOM decomposition.

533   In both incubation experiments, litter is firstly cut into fine fragments and then fully

534   mixed with mineral soil (Recous *et al*.,1995; Guenet *et al*., 2010). Thus, the nutrient

535   accessibility, air permeability and some other environmental factors (e.g. pH) of

536   incubated litter are different from those of decaying litter in more natural,

537   heterogeneous soil conditions. Those different decomposition conditions might be

538   responsible for the differences observed in Fig. 6 between our CUE estimates and

539   previously reported values. We speculate that more heterogeneous conditions reduce

540   nutrient availability and thus might cause lower CUE. Similarly, CUE of surface litter

541   decomposers may be lower than we estimated (Fig. 6), because litter not mixed with

542   soil is probably subject to stronger nutrient limitation.

543   Further validation and development of our model are still necessary to

544	decrease the model uncertainties. Soil mineral N which affects both litter decay rate

545	and CUE of decayed litter is seldom monitored in litter incubation experiments (e.g.

546	Walela *et al*., 2014; Stewart *et al*., 2015) and field litter decay experiments (e.g. Gholz

547	*et al*., 2000; Harmon *et al*., 2009), with few exceptions(Recous *et al*., 1995; Guenet *et*

548	*al*., 2010). An increasing number of land surface models (Wang *et al*., 2010; Zaehle *et*

549	*al*., 2014; Goll *et al*., 2017) have representations of the terrestrial N cycle. By

550	incorporating our newly developed formulations of CUE_d and $f(N_{min})$ in these land

551	surface models that simulate the dynamics of soil mineral N concentration, it will be

552	possible to test and validate our developments with more extensive data from

553	laboratory and field experiments. Moreover, similar to N, P has also been suggested as

554	another important factor for litter decomposition and SOM formation (Güsewell and

555	Verhoeven, 2006; Talkner *et al*., 2009; Manzoni *et al*., 2010; Prescott, 2010),

556	especially in regions with highly weathered soil (Goll *et al*., 2012, 2017; Yang *et al*.,

557	2014). So it might be necessary to include the effects of P on litter decay rate and

558	CUE_d into our model for further decrease the simulation uncertainties.

559

5 Conclusions

561	 By adapting the hypothesis of optimal microbial CUE proposed by Manzoni

562	*et al*. (2017) for use in a CENTURY-based model and also introducing a N scaling

563	function to represent the limits of mineral N availability on litter decay rate, we

564	developed a simple but effective litter decomposition model that accounts for key

565	stoichiometric constraints during decomposition. Validation using observation data

566	obtained from laboratory incubation experiments indicated that our model could well

567	predict the respiration rates of litter in different qualities at various levels of mineral N

568	availability. Idealized simulations using our model revealed that the quality of litter

569	inputs plays an important role in determining the soil C stock at equilibrium.

570	High-quality litter (i.e. with low C:N ratio) tends to form a larger SOM pool as it can

571	be more efficiently utilized by microorganisms than recalcitrant litter (e.g. high C:N

572	ratio). Overall, the developed model captures the microbial mechanisms mediating

573   litter stoichiometry and soil mineral N effects on litter decomposition and SOM

574   formation. Due to the simple and generalizable structure of our model, it can be

575   incorporated into existing land surface models for further long-term and large spatial

576   scale applications.

577

Code and data availability

The CENTURY-based model used here is programmed in MATLAB language. The source code is available online (https://github.com/hchzhang/CENYUTY_CUE/tree/v1.0, DOI: 10.5281/zenodo.1307384). All the data used in this study can be obtained from published literatures. Specific references of these data can be found in section 2.5.

Competing interests

The authors declare that they have no conflict of interest.

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843

844   **Table 1** Optimized parameter values for the five versions of the litter decomposition

845   model used in this study. cue_{fit} is the optimized value of CUE, m_1 and n_1 are the

846   coefficients in Eq. (3), m_2 is the coefficient in Eq. (5), and m_3 is the coefficient in Eq.

847   (6). Values in brackets following each parameter are the means ($\pm$ standard deviations)

848   of the fitted parameter values based on "leave-one-out" cross-validation (see Section

849   2.5 for more details).

Version	CUE	$f(N_{min})$	Parameters
M0	Fixed	1	cue_{fit} (0.57$\pm$0.004)
M1	Eqs. (2), (3)	Eq. (5)	m_1 (0.61$\pm$0.34), n_1 (0.53$\pm$0.21), m_2 (297.4$\pm$38.0)
M2	Eqs. (2), (3)	1	m_1 (0.11$\pm$0.01), n_1 (1.96$\pm$0.13)
M3	Fixed	Eq. (5)	cue_{fit} (0.54$\pm$0.01), m_2 (396.9$\pm$23.6)
M4	Eqs.(2), (3)	Eq. (6)	m_1 (0.13$\pm$0.07), n_1 (1.91$\pm$0.37), m_3 (0.58$\pm$0.12)

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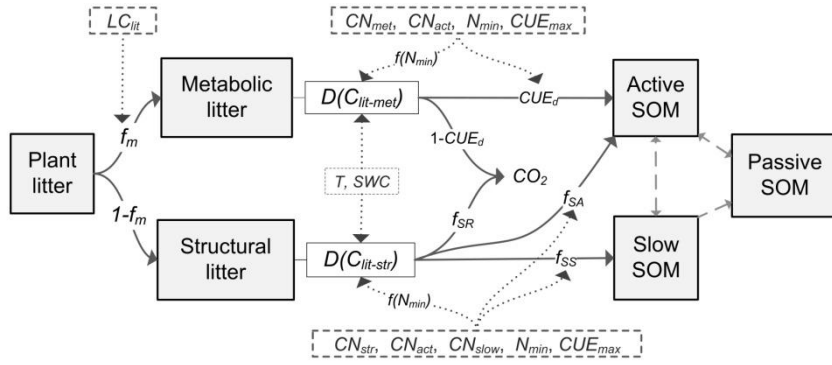
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852 **Figure 1** Schematic diagram of the C flows in the litter decay model used in this study.

853 f_m is the fraction of metabolic compounds in plant litter. $D(C_{lit\text{-}met})$ and $D(C_{lit\text{-}str})$ are

854 the decomposition rates (g C kg^{-1} day^{-1}) of metabolic or structural litter, respectively.

855 LC_{lit} is the lignin:C ratio (on a mass basis) of plant litter; CN_{met}, CN_{str}, CN_{act}, and

856 CN_{slow} are the C:N ratio of metabolic litter pool, structural litter pool, active SOM

857 pool and slow SOM pool, respectively; N_{min} is the concentration of mineral N in

858 solution (g N kg^{-1} soil); $f(N_{min})$ is a factor reducing litter decay rate when soil mineral

859 N availability is limiting; T (°C) and SWC (%) are temperature and soil water content,

860 respectively; CUE_d is C use efficiency of the transformation from litter to soil organic

861 matter (SOM); CUE_{max}=0.8 is the maximum microbial CUE (dimensionless) when

862 growth is limited by C from the organic substrate; f_{SA}, f_{SS} and f_{SR} are the fractions of

863 decomposed structural litter-C that is transferred to active SOM pool, slow SOM pool

864 and released to atmosphere in forms of CO_2, respectively. As in the algorithms in

865 CENTURY model (Parton et al., 1988), here $f_{SA}=CUE_{d\_SA}\times(1\text{-}f_{lig})$, $f_{SS}=CUE_{d\_SS}\times f_{lig}$,

866 $f_{SR}=1\text{-}(f_{SA}+f_{SS})$, where f_{lig} is the lignin fraction (0–1, dimensionless) in the structural

867 litter pool, and CUE_{d_SA} and CUE_{d_SS} are the CUE of C transformation from structural

868 litter pool to active and slow SOM pool, respectively.

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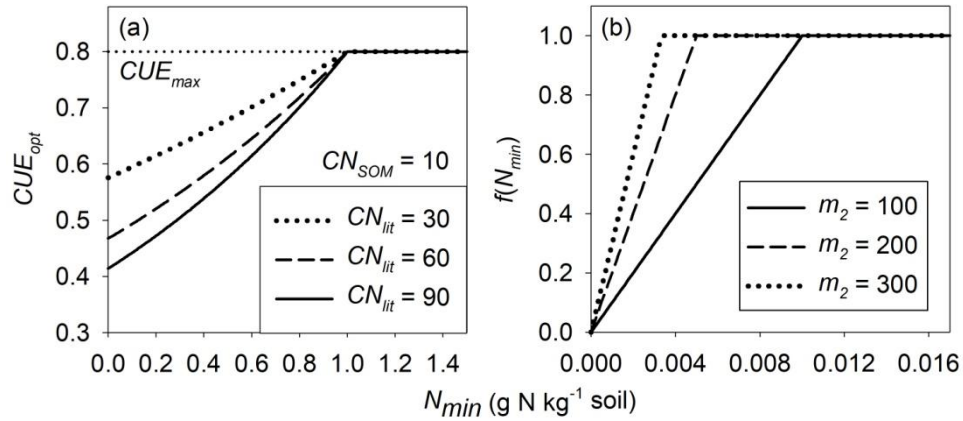
870

871 **Figure 2**. Schematic plot of (a) the optimal carbon use efficiency (CUE_{opt}) as a

872 function of soil mineral nitrogen for different litter C:N ratios (from Eq. (2) in the

873 main text with $m_1 = 0.3$, $n_1 = 1.0$) and (b) the N limitation function $f(N_{min})$ applied to

874 litter decomposition rates (from Eq. (5) in the main text). CN_{lit} and CN_{SOM} are the C:N

875 ratios of the litter and SOM pools, respectively. $CUE_{max} = 0.8$ is the maximum CUE

876 under optimal nutrient condition (C limitation only). m_1 and n_1 are the parameters of

877 Eq. (3) and m_2 is the parameter of Eq. (5).

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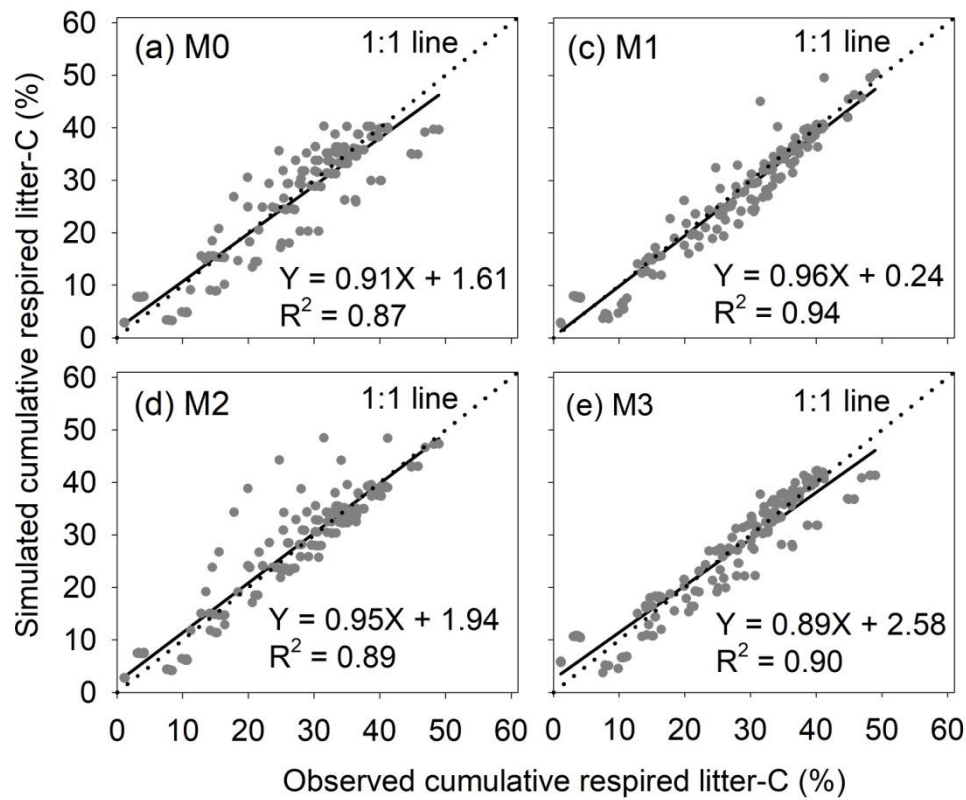
Figure 3 Comparison of the predicted cumulative respired litter-C to observed values
at different times during litter decomposition process. Each dot denotes an
observation of cumulative respired litter-C at a certain day. In total, there are 149
points. M0-M3 are the four versions of litter decay model tested in this study (Table
1).

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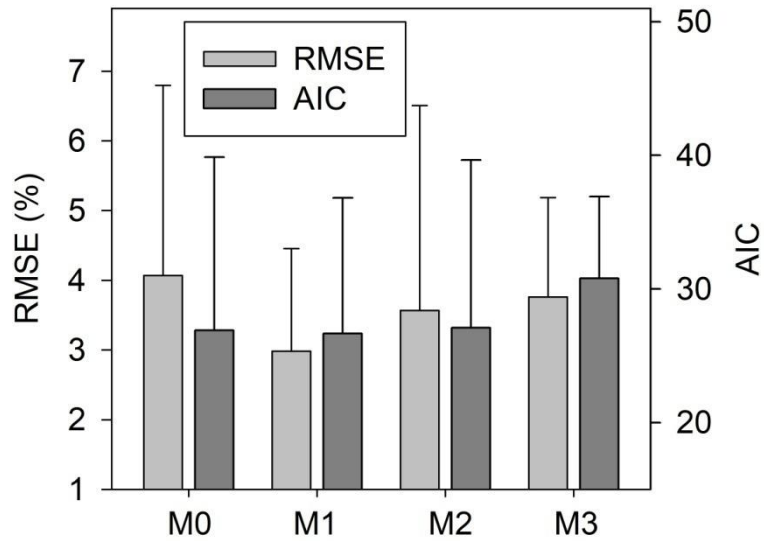
Figure 4 The RMSE and AIC of the simulated cumulative respired litter-C from the

four versions of litter decay model used in this study. Error bars denote the standard

deviation of RMSE or AIC for different incubation experiments. M0-M3 denote the

four models tested in this study (Table 1).

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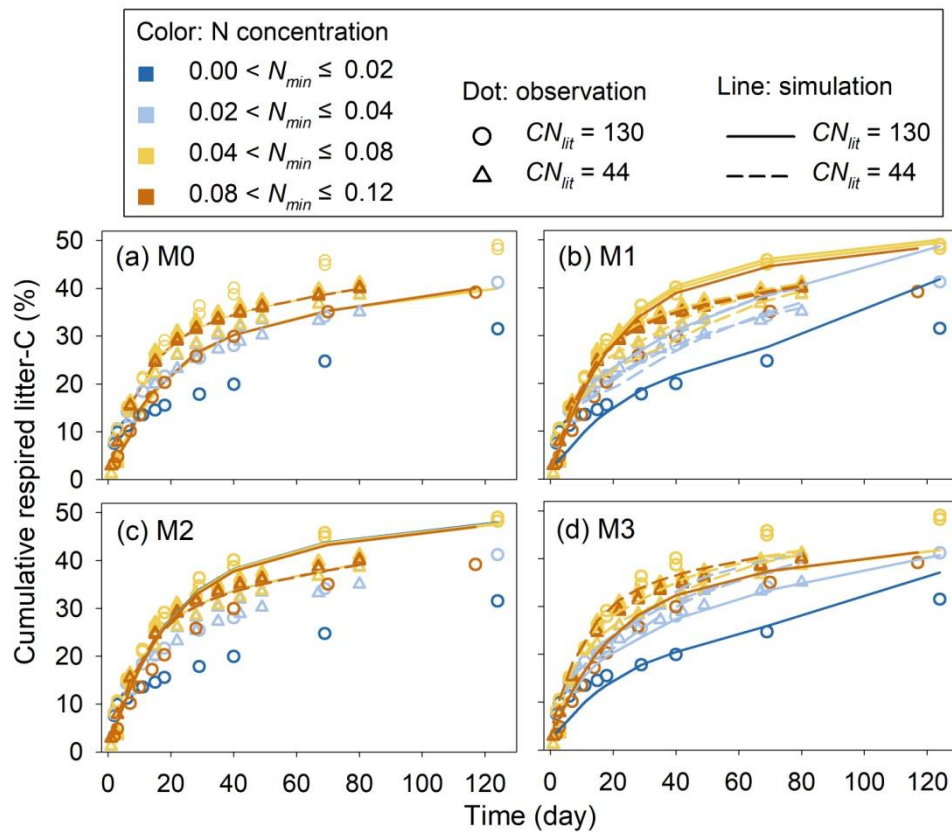
Figure 5 Time series of the simulated (lines) and observed (dots) cumulative respired

litter-C (% of initial litter-C) at four different levels of soil mineral N availability (N_{min},

g N kg^{-1} soil). CN_{lit} is the C:N ratio of plant litter. M0-M3 denote the four models

tested in this study (Table 1). Here the simulation results of each model were

calculated with parameters optimized based on all of the 14 samples of incubation

experiments (Table A2).

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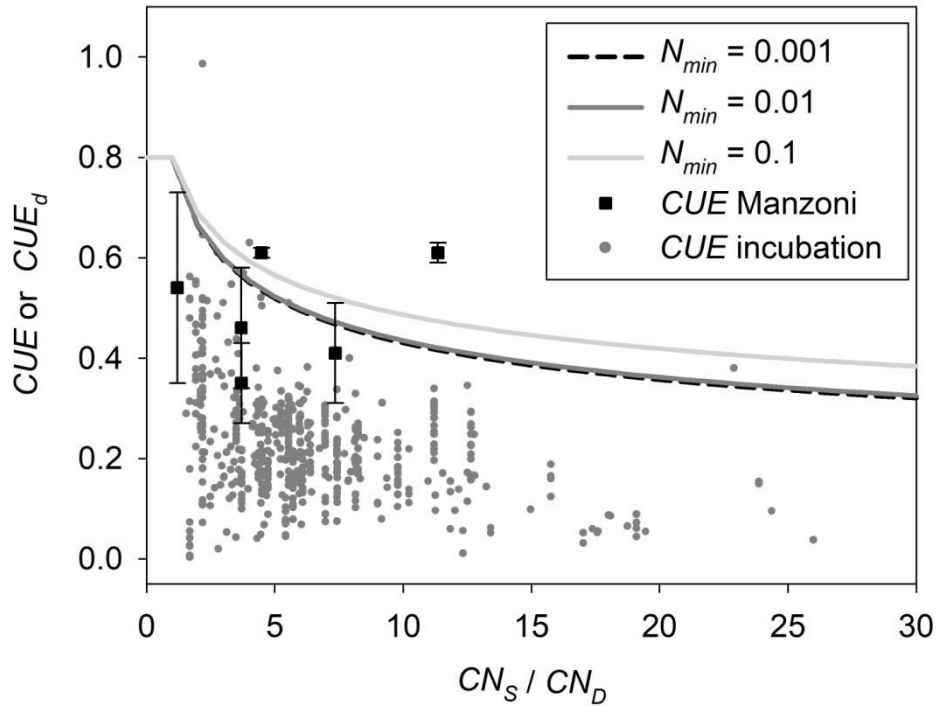
Figure 6 Comparison of CUE_d (lines) predicted by Eq. (2) with parameter values (m_2 = 0.54, n_1 = 0.50) calibrated based on the incubation experiments (Table A2) of Recous et al. (1995) and Guenet et al. (2010)to observed CUE of terrestrial microorganisms along a gradient of CN_S/CN_D. For observed CUE (dots), CN_D and CN_S are the C:N ratio of decomposers and their substrates, respectively. For simulated CUE (lines), CN_S and CN_D correspond to the C:N ratio of donor (litter pool) and acceptor (the active SOM pool of the CENTURY), respectively. Gray dots are the estimated microbial CUE of litter decomposition in natural terrestrial ecosystems from Manzoni *et al*. (2017). Black squares are the microbial CUE measured via laboratory incubation experiments of Gilmour and Gilmour, (1985), Devêvre and Horwáth (2000) and Thiet *et al*.(2006). Error bars represent the standard deviations. N_{min} (g N kg^{-1} soil) is the concentration of soil mineral N.

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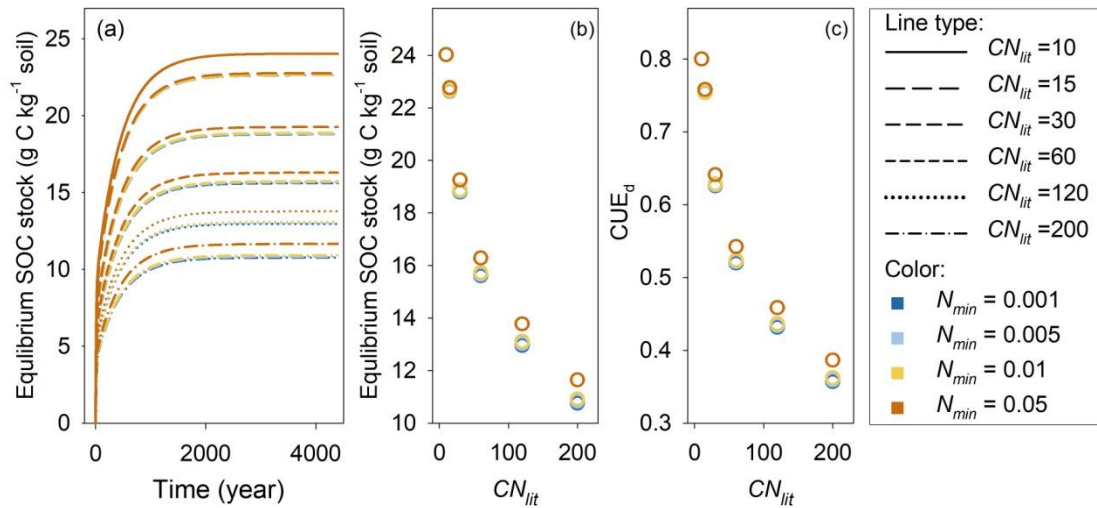
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918 **Figure7** (a) Accumulation of soil organic carbon (SOC) for constant substrates input

919 (plant litter) with different C:N ratios (CN_{lit}) at different levels of soil mineral N

920 concentrations (N_{min}, g N kg^{-1} soil), (b) Change trends of equilibrium SOC stock and

921 carbon use efficiency of decomposed litter (CUE_d) with increasing litter C:N ratio.

922

 Appendix:

 Table A1 List of symbols used in this study; stoichiometric ratios are all expressed on

 a mass basis.

Symbol	Unit	Description
A	g N kg^{-1} soil	Exponent in Eq. (2)
AIC	dimensionless	The Akaike Information Criterion (Eq. (10))
CN_{act}	dimensionless	C to N ratio of active soil organic matter pool
CN_D	dimensionless	C to N ratio of decomposer (Eq. (1))
CN_{met}	dimensionless	C to N ratio of metabolic litter pool
CN_{slow}	dimensionless	C to N ratio of slow soil organic matter pool
CN_{str}	dimensionless	C to N ratio of structural litter pool
CN_S	dimensionless	C to N ratio of substrate (Eq. (1))
C_{lit}	g C kg^{-1} soil	C stock of litter pool (Eq. (4))
CN_{lit}	dimensionless	C to N ratio of litter pool (metabolic or structural, Eq. (2))
CN_{SOM}	dimensionless	C to N ratio of soil organic matter pool
CUE	dimensionless	Microbial carbon use efficiency
CUE_d	dimensionless	Carbon use efficiency of decomposition (C incorporated in SOC over litter C decomposed)
CUE_{fit}	dimensionless	Optimized value of fixed CUE in model M0 and M4
CUE_{max}	dimensionless	Maximum CUE_d (Eqs. (1) and (2))
CUE_{opt}	dimensionless	Optimal CUE_d (Eq. (1))
CUE_{d_SA}	dimensionless	CUE of the transformation from structural litter to active SOM pool
CUE_{d_SS}	dimensionless	CUE of the transformation from structural litter to slow SOM pool
$D(C_{lit-met})$	g C kg^{-1} soil day^{-1}	Decomposition rate of metabolic litter
$D(C_{lit-str})$	g C kg^{-1} soil day^{-1}	Decomposition rate of structural litter
$f(N_{min})$	dimensionless	Limit factor of soil mineral N on litter decomposition (Eqs. (4) and (5))
$f(tem)$	dimensionless	Limit factor of soil temperature on litter decomposition (Eq. (4))
$f(water)$	dimensionless	Limit factor of soil water content on litter decomposition (Eq. (4))
f_m	dimensionless	Fraction of metabolic plant litter
f_{SA}	dimensionless	Fractions of decomposed structural litter-C that is transferred to active SOM pool
f_{SR}	dimensionless	Fractions of decomposed structural litter-C that is released tp atmosphere
f_{SS}	dimensionless	Fractions of decomposed structural litter-C that is transferred to slow SOM pool
I_N	g kg^{-1} soil	Maximum mineral N immobilization rate (Eq. (1))
K	day^{-1}	potential maximum turnover rate (Eqs. (4) and (7))
LC_{lit}	dimensionless	Lignin to C ratio of litter input
m_1	kg g^{-1} N	Coefficients in Eq. (3)
n_1	g N kg^{-1} soil	Coefficients in Eq. (3)
m_2	day^{-1}	Coefficients in Eq. (5)

m_3	kg g^{-1} N	Coefficients in Eq. (6)
N_{min}	g N kg^{-1} soil	Soil mineral N concentration (Eq. (5))
RMSE	%	Root mean square error (Eq.(9))
SOC	g C kg^{-1} soil	Soil organic carbon
SOM	g C kg^{-1} soil	Soil organic matter
U_0	g C kg^{-1} soil day^{-1}	C uptake rate when soil mineral N is fully adequate for litter decay (Eqs. (1) and (8))

926

927 **Table A2** Information about the 14 samples of laboratory incubation experiment used in this study. CN_{lit} and LC_{lit} are the C to N ratio and lignin

928 to C ratio of plant litter, respectively. CN_{SOM} is the C to N ratio of SOM pool. N_{min} is the concentration of soil mineral N (NO_3^- -N + NH_4^+ -N).

929 For the incubation experiments of Guenet *et al.* (2010), cumulative respired litter-C was measured on days 1, 3, 7, 15, 22, 28, 35, 42, 49, 67 and

930 80, and N_{min} was measured on days 3, 7, 17, 28 and 80. For the incubation experiments of Recous *et al.* (1995), both cumulative respired litter-C

931 and N_{min} were mostly measured on days 2, 3, 6, 11, 15, 18, 29, 40, 69 and 124.

Sample	CN_{lit}	LC_{lit}	CN_{SOM}	Initial N_{min} (g N kg⁻¹ soil)	Duration (day)	Temperature (°C)	Soil moisture (%, in volume)	Litter type	Reference
1	44	0.26	11	0.035	80	20	50	Crop (wheat)	
2	44	0.26	11	0.051	80	20	50	Crop (wheat)	
3	44	0.26	11	0.055	80	20	50	Crop (wheat)	
4	44	0.26	11	0.033	80	20	50	Crop (wheat)	Guenet *et al.*,
5	44	0.26	11	0.049	80	20	50	Crop (wheat)	2010
6	44	0.26	11	0.067	80	20	50	Crop (wheat)	
7	44	0.26	11	0.033	80	20	50	Crop (wheat)	
8	44	0.26	11	0.048	80	20	50	Crop (wheat)	
9	44	0.26	11	0.079	80	20	50	Crop (wheat)	
10	130	0.23	9	0.010	124	15	42	Crop (Corn)	
11	130	0.23	9	0.030	124	15	42	Crop (Corn)	Recous *et al.*,
12	130	0.23	9	0.060	124	15	42	Crop (Corn)	1995
13	130	0.23	9	0.080	124	15	42	Crop (Corn)	
14	130	0.23	9	0.100	124	15	42	Crop (Corn)	

932

933 **Table A3** List of parameters calibrated for two versions of the litter decomposition

934 model (M0, M1): k_{litm} and k_{lits} are respectively the turnover rates of metabolic and

935 structural litter pools, m_4 is the coefficient in Eq. (8), cue_{fit} is the optimized value of

936 CUE, m_1 and n_1 are the coefficients in Eq. (3), and m_2 is the coefficients in Eq. (5).

Version	CUE	$f(N_{min})$	Parameters
M0	Fixed	1	cue_{fit}, k_{litm}, k_{lits}, m_4
M1	Eqs.(2), (3)	Eq. (5)	m_1, n_1, m_2, k_{litm}, k_{lits}, m_4

937

938   **Table A4** Specific setting of litter and SOM properties, and soil conditions in the 16

939   idealized simulations for exploring the impacts of litter stoichiometry (i.e. C:N ratio)

940   and soil mineral N on SOC accumulation. CN_{lit} and LC_{lit} are the C to N ratio and

941   lignin to C ratio of plant litter, respectively. Lit_{inp} (g C kg^{-1} soil day^{-1}) is the daily input

942   rate of plant litter. CN_{SOM} is the C to N ratio of SOM pool. N_{min} (g N kg^{-1} soil) is the

943   concentration of soil mineral N (NO_3^- -N + NH_4^+ -N). *Tem* (°C) and *SWC* (%) are the

944   temperature and soil water content, respectively.

Experiment	CN_{lit}	LC_{lit}	Lit_{inp}	CN_{SOM}	N_{min}	*Tem*	*SWC*
1	15	0.2	0.006	12	0.001	25	60
2	30	0.2	0.006	12	0.005	25	60
3	60	0.2	0.006	12	0.01	25	60
4	120	0.2	0.006	12	0.05	25	60
5	15	0.2	0.006	12	0.001	25	60
6	30	0.2	0.006	12	0.005	25	60
7	60	0.2	0.006	12	0.01	25	60
8	120	0.2	0.006	12	0.05	25	60
9	15	0.2	0.006	12	0.001	25	60
10	30	0.2	0.006	12	0.005	25	60
11	60	0.2	0.006	12	0.01	25	60
12	120	0.2	0.006	12	0.05	25	60
13	15	0.2	0.006	12	0.001	25	60
14	30	0.2	0.006	12	0.005	25	60
15	60	0.2	0.006	12	0.01	25	60
16	120	0.2	0.006	12	0.05	25	60

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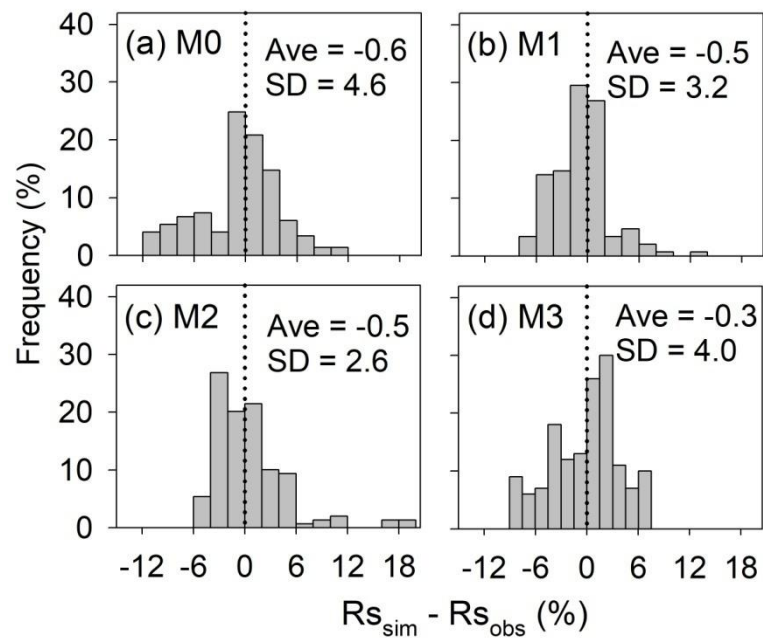
Figure A1 Distribution of the difference between the predicted cumulative respired

litter-C (Rs_{sim}, %) and the observed values (Rs_{obs}, %) for all experiments and points in

time. SD is standard deviation of the biases. M0-M3 denote the four models tested in

this study (Table 1).

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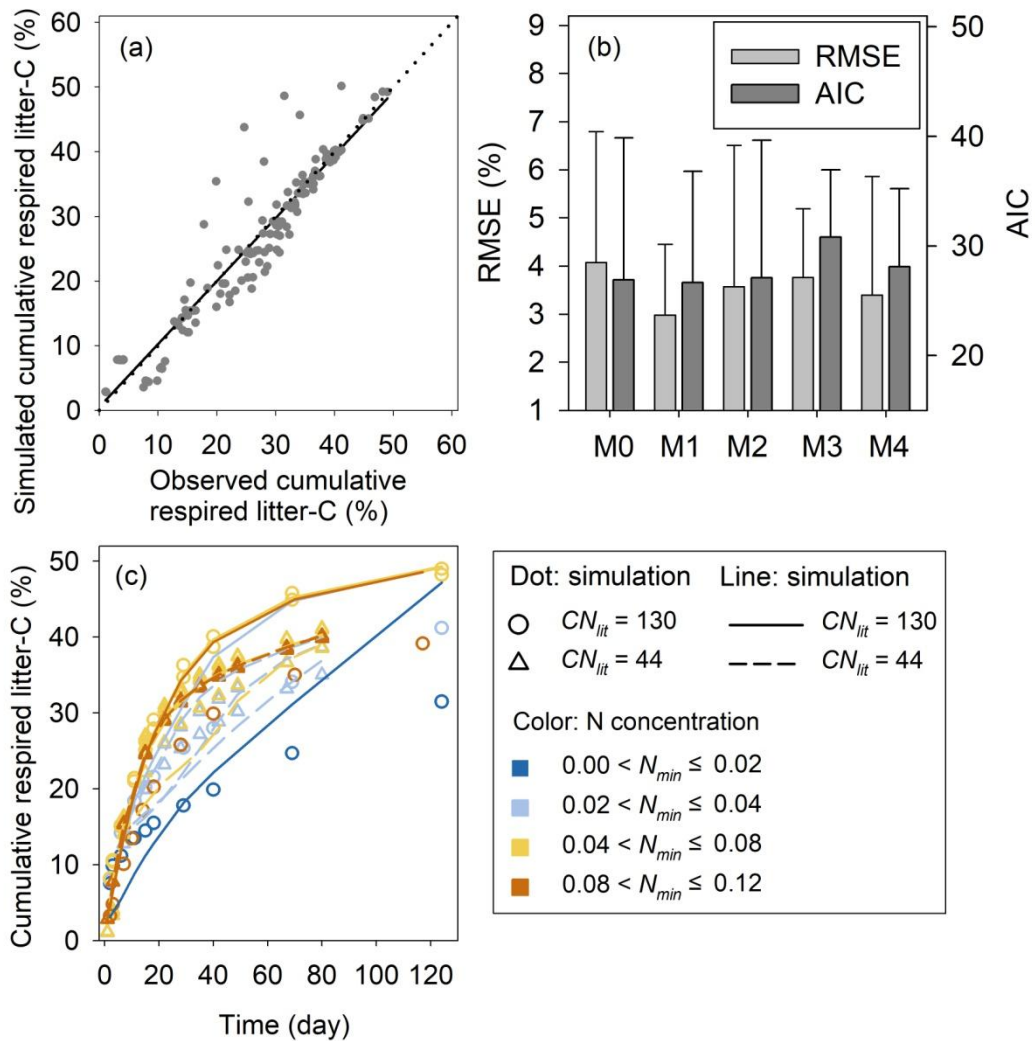
Figure A2 Comparison between simulated cumulative respired litter-C with $f(N_{min})$

(inhibition effect of soil mineral N on litter decomposition) calculated by Eq. (6) and

the observed results from incubation experiments. In figure (b), M0-M4 denote the

five versions of litter decay model in Table 1. M4 denote the model which used Eq. (2)

to calculate the dynamic CUE and Eq. (6) to calculate $f(N_{min})$.

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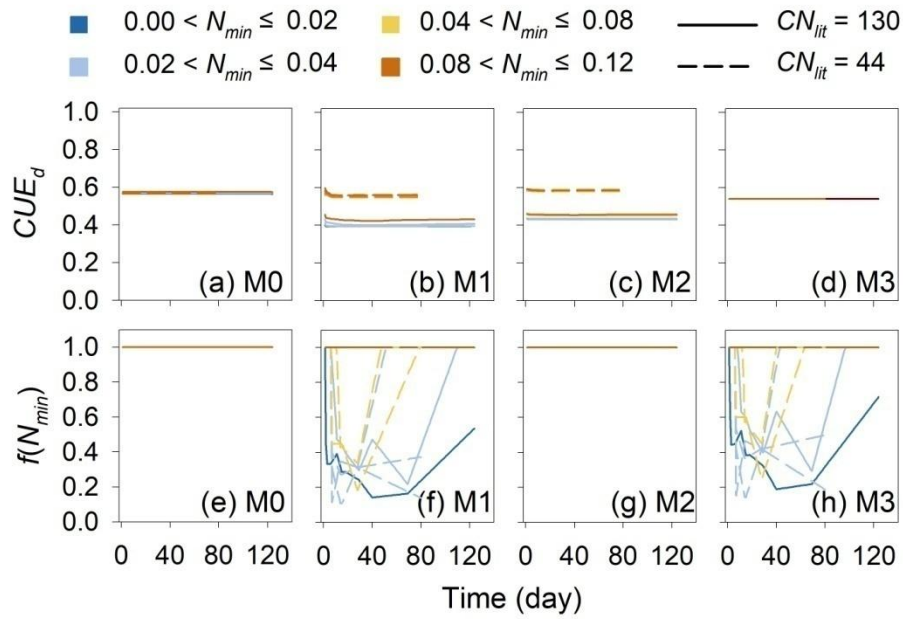
960

961   **Figure A3** Dynamic of the simulated carbon use efficiency (*CUE*) and $f(N_{min})$ during

962   the incubation experiments (Table A4). CN_{lit} is the C:N ratio of incubated litter, and

963   N_{min} is the initial soil mineral N concentration (g N kg^{-1} soil). M0-M3 are the four

964   models in Table 1. Here the simulation results of each model were calculated with

965   parameters optimized based on all of the 14 samples of incubation experiments (Table

966   A2).

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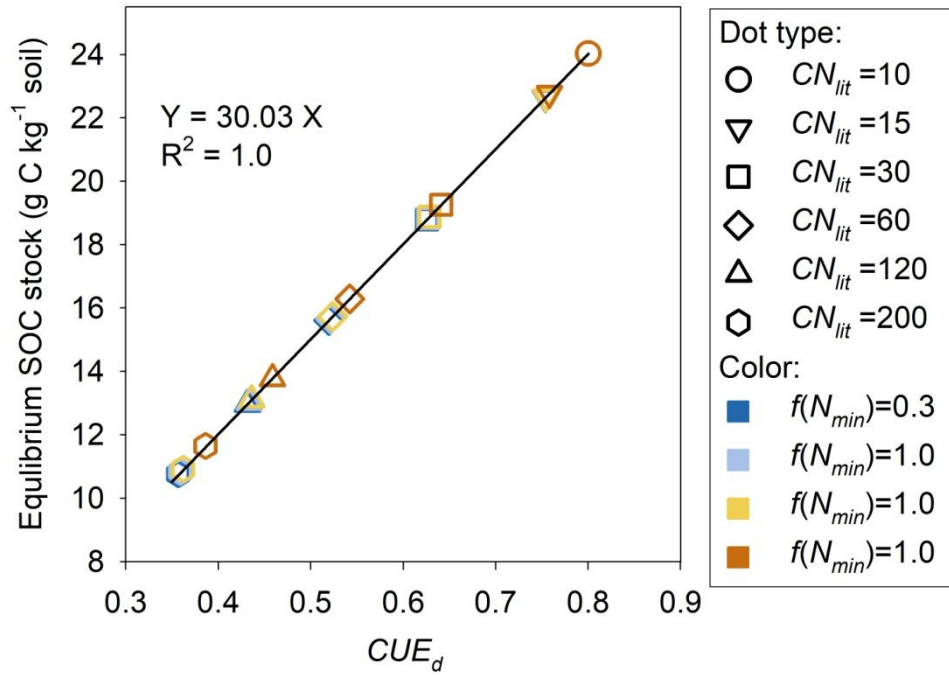
968

969 **Figure A4** Relationship between C stock of the potentially equilibrated SOM pool

970 and the carbon use efficiency of decomposed metabolic litter (CUE_d) at the dynamic

971 equilibrium stage. $f(N_{min})$ denote the inhibition factor (0–1) of soil mineral N on litter

972 decomposition.

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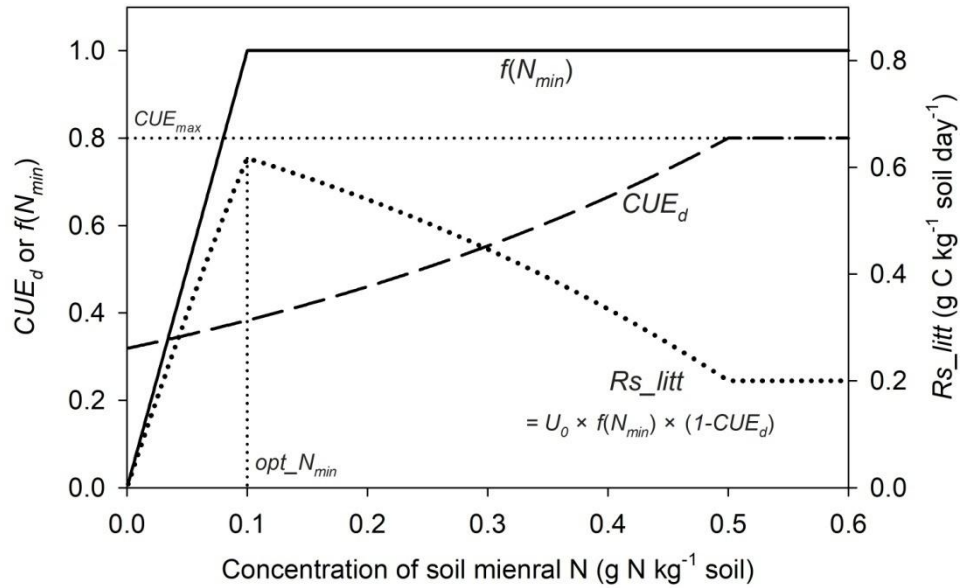
Figure A5 Schematic plot for change trends of $f(N_{min})$ (inhibition effect of mineral N,

Eq. (6)), CUE_d (carbon use efficiency of decomposed litter, Eqs. (2), (3)) and Rs_litt

(litter respiration rate) with increasing concentration of soil mineral N. CUE_{max} (= 0.8)

is the maximum CUE set in this study. opt_N_{min} denotes the concentration of soil

mineral N at which litter respiration is maximized. U_0 is the potential decomposition

rate when mineral N is fully adequate for litter decay.