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C dynamics modelling of peatland plant litter

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SG wrote the article, developed and implemented the model and participated in the design of the experiment, the data acquisition and the discussion. NG was in charge of the day-to-day management of the experiment, the regular data acquisition, participated in the design of the experiment and the analysis of the data. FLD participated in the design of the experiment and the discussion. A-JF contributed to the writing of the article, participated in the discussion and the improvement of the modelling. FD participated in the implementation of the carbohydrate and the $SUVA_{280}$ analyses and the discussion. NL participated in the implementation, the quantification and discussion of the carbohydrate analyses.

Abstract

C dynamics in soils plays an important role in the interactions between climate and terrestrial ecosystems. Given the importance of the soil C pool in future climate scenarios, accurate models are required which can then be integrated into global models. On the one hand, models of soil C dynamics can be very simplistic in that only solid organic matter (OM) is taken into account with constant rates. Such models can miss important features of soil C dynamics such as enzymatic activity and CO_2 production. On the other hand, some models are too complicated to be experimentally calibrated, tested and widely used. We propose a model of soil C dynamics that (i) integrates all C fluxes from the solid to the gaseous form, and (ii) can be easily implemented experimentally. Because peatlands are important C stores that are experiencing vegetation changes, the model was tested on experimental results obtained with peatland litter: *Sphagnum cuspidatum* (autochtonous vegetation), *Molinia caerulea* and *Betula* spp (both invasive species).

Our model was able to accurately describe the early stages of C dynamics in litter especially when only one pool of OM was used and when catalysis and respiration rates were allowed to decrease with time. Our model is efficient in assessing the entire actual catalysis rate. This is a notable achievement as usually, enzyme activity is measured on specific enzymes in conditions often far from actual ones. Our model appeared to be sufficiently robust and worthy of development, keeping in mind that it should remain experimentally testable.

Keywords: Exo-enzyme activity, *Sphagnum cuspidatum*, *Molinia caerulea*, *Betula* spp, soluble carbohydrates, Water Extractable Organic Carbon.

Introduction

Peatlands are characterized by an imbalance between productivity and decomposition, leading to organic matter (OM) accumulation and long-term C-sequestration in peat (Clymo, 1984; Gorham 1991). The chemical characteristics and degradation pathways of plant litter involved in peat accumulation are multiple. In subtropical peatlands, lignin-derived OM plays a major role in determining the imbalance between primary production and decay. In high latitude *Sphagnum*-peatlands, the complex combination of processes involving both polysaccharides (van Breemen, 1995; Hájek et al, 2011) and polyphenols (Freeman et al., 2001) certainly explain the very efficient C storage capacity of these ecosystems. Chemical characteristic differences in the context of climate change are not trivial as the decomposition rates of different classes of biopolymers have different temperature sensitivity (Davidson and Janssens, 2006; Berg and McClaugherty, 2008; Siegenthaler et al, 2010). Compounds with higher activation energy, such as lignin, should have higher temperature sensitivities than compounds with lower activation energy, such as cellulose (Davidson and Janssens, 2006). As the decomposition process in peatland may respond differently to environmental changes depending on the litter biochemical composition (Davidson and Janssens, 2006; Hajek et al, 2010), storage capacity of *Sphagnum* peatlands may be greatly affected. Furthermore, it has been observed in these systems that vascular plants dominance is increasing at the expense of *Sphagnum* species due to human disturbances (Francez and Vasander, 1995; Berendse et al, 2001; Bubier et al, 2007). The shift in biodiversity and plant functional groups *(Sphagnum vs* vascular plants) may also imply a shift in litter OM dynamics with an increase in lignin-controlled decomposition over *Sphagnum* polysaccharides and polyphenols control.

The litter decomposition rate is generally assessed using litter bags or respirometry by measuring the remaining mass of OM and elements such as C and the amount of C that has been evolved to CO_2 or CH_4, respectively (Johnson and Damman, 1993; Francez 1995; Verhoeven and Toth 1995; Cotrufo et al, 2010; Grover and Baldock 2010). Mass loss and gaseous C release kinetics modeling depends on the underlying hypothesis concerning the pools of C or nutrients and their decomposition rates. The most simple first-order kinetics model assumes a single constant (Stanford and Smith, 1972). Other models use two-pools of OM types with different decomposition rates. The latter corresponds much better to the processes of C or nutrient release in the soil (Andrén and Paustian 1987; Wieder and Lang, 1982; Latter et al 1997). These models have been extensively used in peatlands (Updegraff et al, 1995; Latter et al, 1997; Andersen et al, 2008) and proved to well describe the fate of litter C after litter fall (Zhang et al, 2008; Prescott, 2011). Whether one or two pools connected or not, and variation

in decomposition rates over time are not often considered (Wieder and Lang 1982; Moorhead et al. 1996; Rovira and Rovira, 2010). Furthermore, the rates of mass loss and C release result from different processes (solubilisation by exo-enzyme activity and microbial respiration, respectively), operating at the biochemical and microbial levels. These processes need to be understood in order to improve the development of decomposition models and the prediction of ecosystem responses to global change (Sinsabaugh et al, 2002). For this reason, exo-enzyme activity and the pools of Dissolved Organic Carbon (DOC) or Water Extractable Organic Carbon (WEOC, which is part of the Water Extractable Organic Matter or WEOM) in soil have received increasing attention in the last decade (Criquet et al, 2001, Sinsabaugh et al 2002; Fenner et al, 2005, Kalbitz et al 2006; Gauthier et al 2010). Most studies on exo-enzyme activities have been undertaken with simple substrates (small molecules) found in saturation, whereas in natural conditions OM consists mainly of high molecular weight organic polymers (Wallenstein and Weintraub, 2008). In addition to the soluble products of exo-enzyme activities on polymeric substances, the water soluble fraction also contains biological compounds such as root exudates, animal excretion and microbial products (Paul and Clarke, 1996). Once soluble, the organic C can be consumed and respired by the microorganisms. Recently, Gauthier et al (2010) concluded from field and laboratory experiments that the WEOC of surface soils in forest ecosystems mainly originates from the vegetation via litter leachates. Total organic C and soil organic C (SOC) pools have been widely studied in peatlands, but WEOC which is likely the most labile and mobile fraction of SOC has received much less attention (Delarue et al, 2011).

The aim of this paper was to develop a dynamic model i) to simulate and predict the short-term dynamics of C-litter, ii) to propose a simple tool to estimate the actual global enzyme activity leading to the fresh OM decomposition and iii) to test in this model how the WEOC pool could react to changes in catalysis and respiration rates. The innovative feature of the model is that it considers measurable fluxes of C from the solid to the soluble and gaseous phases all at the same time, which, when implemented experimentally, gives the actual rates of decomposition through enzyme activity and respiration simultaneously. In order to calibrate our model, we carried out a laboratory experiment with monospecific litters to obtain an integrated view of C-litter decomposition and mineralization. We used three chemically contrasting litters (*Sphagnum,* leaves of *Molinia* and *Betula* spp) and measured the fate of initial C-litter into solid (labile and recalcitrant compartments), water-soluble and gaseous forms over 46 days incubation time. To validate our model, we compared the results of a litter mixture experiment with the same litter to the results obtained with the model.

Materials and methods

Model description

A simple mass balance model was built, composed of three compartments corresponding to the solid, aqueous and gaseous forms of C: (i) the Litter C: L, (ii) the Water Extractable Organic Carbon (WEOC): W and (iii) the cumulative C-CO_2 respired: G (Fig. 1, formula 1). The amount of C in each compartment was expressed as part of the initial C of the litter (g of C in a compartment per g of initial C content of the litter: g C g^{-1} initial C in litter).

$$L_{t0} = L_{ti} + W_{ti} + G_{ti} = 1 \quad (1)$$

with i the time (day), L_{ti}: the remaining litter C at time i, W_{ti}: the WEOC at time i, G_{ti}: the cumulative C-CO_2 produced from time 0 to time i.

Fluxes of matter from one compartment to another were achieved by process rates. The C from the litter (L, Fig. 1) flows into the WEOC compartment (W, Fig. 1) at a rate “c”. The litter decomposition through the enzyme catalytic reactions “c” represent the attack of the solid C by exo-enzymes Simultaneously, the WEOC is taken up and respired at the rate “r” by the microorganisms and released out of the system in the gaseous form of CO_2 and cumulated over time (G, Fig. 1). These rates were expressed as the fraction of the C of the litter pool that has been catalyzed per unit of time (in g C g^{-1} remaining C in litter day^{-1}). The respiration rate r was expressed as the fraction of the C of the WEOC that has been respired from the amount of WEOC present per unit of time (g C g^{-1} WEOC d^{-1}). The C lost through respiration was calculated by integrating the average CO_2 production between t and t_{+1} and then summing up over time. Differential equations were found to be the best mathematical formalism to model the mass flow (Manzoni and Porporato, 2009):

$$dL/dt = -cL \quad (2)$$

$$dW/dt = cL - rW \quad (3)$$

These equations were integrated to obtain the pool content at time t:

$$L = L_0 e^{-ct} \quad (4)$$

$$W = (cL_0/r\text{-}c)e^{-ct} + \alpha e^{-rt} \quad (5)$$

α was determined at t = 0:

$$\alpha = W_0 - (cL_0)/(r - c) \quad (6)$$

As L and G can be calculated at any time, G is deduced from the mass conservation equation (eq. 1).

The model was run with two different rate functions with time: (i) all rates were considered constant with time and (ii) the rates were allowed to decrease with time in a negative exponential way. In the 1 pool model, OM is taken as a whole and decreasing reaction rates could reflect changes in

decomposing OM reactivity (Rovira and Rovira, 2010). We used the equations calculated by Rovira and Rovira (2010) for instantaneous rates (equations 7 and 8) and their integration (equation 9 and 10) which replaced c and r in equations 4 and 5 as proposed by Rovira and Rovira (2010):

$$c(t) = a_c + b_c e^{-m_c t} \quad (7)$$

$$r(t) = a_r + b_r e^{-m_r t} \quad (8)$$

$$\int c(t) = a_c t - (b_c/m_c)(e^{-m_c t} - 1) \quad (9)$$

$$\int r(t) = a_r t - (b_r/m_r)(e^{-m_r t} - 1) \quad (10)$$

with $a_c + b_c$ and $a_r + b_r$ initial values of catalysis and respiration rates respectively, and $m_{c,}$ and m_r the rates at which the solid OM catalysis and respiration rates decrease over time. Here, solid OM catalysis referred to the activity of exo-enzymes excreted by microorganisms (Schimel and Weintraub, 2003). Abiotic factors, such as light, can affect solid and dissolved OM breakdown (Austin and Vivanco, 2006; Köhler et al., 2002). However, as all samples were kept in the dark, abiotic catalysis should certainly not occur.

To test whether a 2 pool model with constant values would better describe the early litter C dynamics than a one pool model with decreasing rate, the L pool was divided into a labile (LL, equation 11) and recalcitrant pool (RL, equation 11):

$$L_{ti} = LR_{ti} + LL_{ti} \quad (11)$$

The equations 4 and 5 were rewritten in consequence, with c1 the catalysis rate for the more labile litter fraction) and c2 the catalysis rate for the more recalcitrant litter fraction. The terms “labile” and “recalcitrant” are used in a relative sense. In the early stage of decomposition studied here, the more labile litter pool LL is assumed to be composed of macromolecules, which do not constitute the plant tissue, such as plant debris and cellular remains of dead microbes and plants (Berg and McClaugherty, 2008). This pool is assumed to be labile because it is considered to be nutrient rich and has a high specific surface that increases enzyme catalysis (Berg and McClaugherty, 2008). The recalcitrant pool is composed of the different biopolymers constituting the plant tissues (hemicellulose, cellulose, cutin, suberin, and polyphenols). Humic substances constitute another pool that is even more recalcitrant, but this was not taken into account as the humification process occurs on a longer time scale than the model and experiment presented here (Berg and McClaugherty, 2008).

Model calibration, testing and validation

Calibration - To calibrate the model, we used a mono-specific litter average data set originating from a laboratory experiment. The mass remaining, the WEOC and the CO_2 production were estimated in

three chemically contrasted litters: *Sphagnum cuspidatum*, *Betula* spp (*B*. *pubescens*, *B*. *pendula* and hybrids are present on the study site) and *Molinia caerulea* litters. For *Sphagnum cuspidatum*, the light brown part between the green and the well humified brown parts was used as litter. The *Betula* spp and *Molinia caerulea* litters always consisted in their leaves. *Sphagnum* species have high carbohydrate and low N contents, *Betula* litter has low carbohydrate and high N contents and *Molinia caerulea* litter has median carbohydrate and low N contents (Table 1, Jia et al, 2008; Gogo et al, 2011). The litters were collected in the field in La Guette peatland, 100 km South of Paris, France (154 m, 47°19', North and 2°14' East, Gogo et al, 2011). The model was computed using an Excel spreadsheet. The parameters of the models were optimized by minimizing the Root Mean Square Error (RMSE).

Test of sensitivity - Sensitivity was tested on one type of model: 1 pool, Negative exponential decrease of reaction rates. The reference parameters were: a_c = 0.002, b_c = 0.002, m_c = 0.05 for solid OC decomposition and a_r = 0.02, b_r = 0.9, m_r =0.01. The tests consisted in varying (i) the catalysis parameters alone, (ii) the respiration parameters alone and (iii) all parameters. Four scenarios were tested:

- two maximizing scenario where a and b parameters were increased and m parameters were decreased by (i) 10% and (ii) 50% of their reference values to simulate an overall activation of C dynamics,
- two minimizing scenario where a and b parameters were decreased and m parameters were increased by (i) 10% and (ii) 50% of their reference values to simulate an overall inhibition of C dynamics.

Validation - To validate the model, a complementary experiment was undertaken with mixed litter in equal proportions: *S.cuspidatum* with *Betula*, *Betula* with *Molinia* and *Molinia* with *S. cuspidatum*. For each mixture of litter, a set of average model parameters was calculated from the calibration with the litter incubated alone. The model was run with these averaged parameters and the modeled L, W and G data were compared to the observed data using regression.

Experimental set up and response variables

Set up - A total of 63 samples were prepared (3 litter types, 21 samples per litter type) and incubated in controlled environmental conditions. This led to a kinetic study of 7 dates with 3 replicates of each litter type, which were randomly retrieved at each date i.e. 2, 6, 13, 20, 27, 34 and 46 days of incubation. The litters were air dried until they reached a constant weight. Surface peat water was

collected from the same site. The day after the water was collected, air dried litter samples were weighed and inoculated with 20 ml peat water overnight. Then, the excess water of the litters was removed with a tissue and the litters were placed in a 50 ml tube, which contained 5 ml of a potassium sulfate saturated solution (120 mg l^{-1}) to maintain the relative humidity (Aerts and de Caluwe, 1997). Glass marbles were also placed at the bottom of the tube and covered with a PVC filter (0.5mm mesh) to avoid contact between the litter and the potassium sulfate solution. An insulated container (0.3m x 1m x 1m) ensured constant environmental conditions during the incubation. To obtain a water-saturated air, the atmosphere of the container was filled with air that was pumped through warm water. Temperature and humidity were monitored and showed that the experimental setup ensured a constant water-saturated atmosphere and an air temperature of 22.5 ± 0.3.°C (n = 32). Immediately after removal of the sample, the CO_2 production was measured. Then water extraction was undertaken and finally the sample was dried at 50°C during 48 H before weighing.

CO_2 production - The tubes were placed during 20 to 30 minutes (depending on the CO_2 production rate) in a chamber. The cover of the chamber was fitted with a mounting flange, which could receive a Vaisala CO_2 probe (GMP343). The CO_2 concentrations were monitored and recorded directly on a computer. The CO_2 production was calculated from the slope of the increasing concentration in time.

Water Extractable Organic Carbon (WEOC), aromaticity and carbohydrates - After measurement of the CO_2 production, the litter was taken out of the tube and placed in an aluminum cup with 20 ml of deionized water at room temperature. The litter was rinsed and the extract was filtered (0.45 µm). The litter was rinsed again with 10 ml of deionized water to ensure complete extraction of soluble organic C and the extract was filtered (0.45 µm). On the three replicates, one was randomly dedicated to carbohydrate analysis and the two remaining samples were used for DOC analysis (Shimadzu TOC 5000) and UV analysis (Hitachi U-1100), which allowed Water Extractable Organic Carbon (WEOC in g C g^{-1} initial litter dry weight) and Specific UV Absorption at 280 nm ($SUVA_{280}$ in l mg^{-1} cm^{-1}) to be calculated. Before injection into the Shimadzu TOC 5000, the samples were acidified and bubbled to eliminate dissolved inorganic C, leaving only the DOC to be analyzed. The $SUVA_{280}$ informs on the aromaticity of the DOC (Chin et al, 1994; Delarue et al., 2011).

The sample for carbohydrate analysis was dried with a rotary evaporator. Then, the carbohydrates were dissolved in pyridine. After methylation with BSTFA at 60°C during 1h, the samples were injected into a Perkin Elmer GC. Deoxy-glucose was used as standard (see Delarue et al, 2011, for further details).

Mass of litter remaining and OM quality - After the WEOC procedure, the remaining litter was dried at 50° C during 48 hours and weighed. Initial air dried samples of each litter were also dried in the same way. This allows calculation of the oven dried weight of the incubated air dried samples and calculation of the oven dried mass loss. Elemental contents (C, H, N) were measured (EA Flash Thermo) on the litter from days 0, 13 and 46. The results showed that the proportion of C to the total mass remained relatively constant over time for all litter types. Then, the loss on ignition of all the samples was undertaken to measure the OM content and the C content of each litter was estimated to be half of the OM content. The litter particle left on the filter was not weighed with the rest of the remaining mass. These particles left on the filter were part of the litter compartment (L_t in formulas 1 and 2, and in Fig. 1). The experimental setup allowed estimation of the litter compartment as it corresponds to the missing mass in the mass balance calculation. Because of the conservation of mass (formula 1), this fraction can be calculated by the difference between the initial total C mass and the sum at each date of the C from the measured (i) remaining mass, (ii) WEOC and (iii) C lost through respiration. The mass calculated in this way was added to the mass remaining to form the "L" mass compartment. The initial and final OM quality was assessed with Rock Eval pyrolysis (Disnar et al, 2003). OM pyrolysed during the beginning plateau at 200°C corresponds to free hydrocarbons (Lafargue et al, 1998). The ratio of the peak area during this plateau to the area of the whole pyrogram is named R200. The difference in the R200 ratio between the start and the end of the experiment is assumed to fairly represent the proportion of the most labile fraction: 0.01 for the *Betula* spp litter and 0.04 for the *Sphagnum cuspidatum* litter. In the *Molinia caerulea* litter, as there was no significant difference between the R200 at the start and at the end of the experiment, it was thus assumed that there was no labile C pool in this litter.

Statistics

One-way ANOVAs were performed to test differences in mass loss, WEOC content and CO_2 production between the different litters. Linear regressions between simulated and observed data were conducted to evaluate the performance of the model in the validation procedure.

Results

Model calibration with a single litter experiment

The experimental results showed that the *Betula* litter tended to decay faster and to produce more CO_2 than the *Sphagnum* and *Molinia* litters (Table 2; Fig. 2abc and ghi, respectively). These two litters contained more WEOC than the *Betula* spp litter (Table 2; Fig. 2def).

In the "1 pool" configuration, allowing the reaction rates to decrease improved the overall adjustment of the model to the measured values for all types of litter (Table 3). This was particularly true when both rates were allowed to decrease (Table 3).

Increasing the number of OM pools in the model did not improve the description of the measured values in the *Betula* litter (Table 3). In the *Sphagnum* litter, the adjustment of L (solid C) and G (gaseous C) was slightly improved compared to the 1cNe+rNe model with decreasing rates (Table 2). However, this was possible at the expense of the adjustment of W (liquid C; Table 3). The 1cNe+rNe gave the best overall goodness of fit (Table 3).

The model parameters obtained with the 1cNe+rNe model showed that exo-enzymes catalysis rates presented different patterns in the different litters. In *Sphagnum*, the initial rate (a_c+b_c) was high, but it decreased very rapidly (high m_c; Table 4; Fig. 3a). In *Betula*, the initial rate (a_c+b_c) was also high, but its decrease was an order of magnitude lower than in *Sphagnum* (low m_c; Table 4; Fig. 3a). In the *Molinia*, the initial exo-enzyme catalysis rate and its decrease rate were both very low (Table 4; Fig. 3a). For the respiration, *Sphagnum* and *Molinia* followed the same pattern, with low initial rates and high decreasing rate (Table 4; Fig. 3b). *Betula* had a high respiration rate that decreased slowly with time (Table 4; Fig. 3b).

Sensitivity test of the model

The effect of maximizing and minimizing the catalysis rate had only a minor effect on short term mass loss (maximum 8.8% shift from the reference value after 46 days, Fig. 4a). However, it had a marked effect on both W and G (Fig. 4dg). Tuning respiration rate parameters had more effect on W than on G (Fig. 4beh). After 46 days, a decrease of 4.3% in G was accompanied by an increase of 151% in W. When all parameters were tuned together (Fig. 4cfi), it appeared that W was "buffered": the strong increase or decrease of W caused by catalysis parameter changes was compensated by a respective increase or decrease in respiration rate (Fig. 4f).

Model validation with a mixture of litter

Using the parameters obtained during the calibration step with monospecific litter, a set of theoretical parameters was calculated to predict L, W and G in mixed litters. These predicted values were

compared to the measured values (Fig. 5). The results showed that L (Fig. 5abc) and G (Fig.5ghi) were well predicted by the model (all R^2>0.94 and slope no more than 1 + 0.15 and less than 1 - 0.06, Fig. 5, all correlations were significant). W in both mixtures with the *Betula* spp was the least accurately predicted variable (Fig. 5ef).

Aromaticity and carbohydrates

In the WEOM extracted from the three litters, carbohydrates tended to increase toward the end of the experiment (Table 5). Aromaticity of the WEOM was much greater in the *Molinia* litter than in the *Sphagnum* litter (Fig.6). WEOM aromaticity of *Betula* litter was found in between the two other litters (Fig. 6). For all litters, aromaticity of the WEOM tended to decrease (Fig. 6).

Discussion

Actual catalysis rate assessment

Understanding the C dynamics during decomposition could be improved by incorporating an enzymatic catalysis rate in models (Wallenstein and Weintraub, 2008). Following Schimel and Weintraub (2003), the model proposed in our study assumes that solid OM is solubilised by enzymatic activity. Usually, potential (and not actual) enzymatic activities are assessed by measuring the catalysis reaction of selected enzymes (e.g. beta-glucosidase) on an artificial soluble substrate bearing a fluorophore (usually 4-methylumbelliferyl or MUF). Although this method gives valuable information on specific activities, it has many drawbacks, reviewed by Wallenstein and Weintraub (2008). One of the greatest disadvantages of such a method is the type of substrates used. Indeed, they are simple soluble molecules, whereas in soil the real substrates are long and complex organic polymers such as cellulose and lignin. As suggested by Wieder and Lang (1982), fitting mathematical models to data is an appropriate way to determine the rate constant. The results of the calibration and validation procedures, by fitting simulated to experimental data, showed that our simple model is able to assess the actual exo-enzyme catalysis rate and how it changes over time. This was made possible by modelling not only the mass loss or the CO_2 evolved separately, but by linking these two variables with the intermediate WEOC compartment. As pointed out by Cotrufo et al. (2010), knowledge of the proportion of all the C compartments is still lacking in order to better understand how the different C pools interact. Because it is easily implemented experimentally, our model was able to grasp the C dynamics measured in three chemically contrasted litters. This shows that our model can be a

valuable tool to give an account of the effect of treatments (e.g. mineral N pulse, a sudden change in temperature or humidity) on each of the proportions of C pools and on the rates they depend on.

The WEOC pool: the most sensitive and dynamic compartment

The model investigated in this study postulated that the WEOC pool is controlled by an input rate (enzymatic catalysis) and an output rate (respiration). Thus, WEOC is a transitory compartment that is influenced by both processes. Although, the importance of the transitory nature of this pool and its turnover is acknowledged (Schimel and Weintraub, 2003), most studies used a reductionist option considering WEOC either as a C source (e.g. Bowen et al, 2009) or as a C sink (e.g. Kalbitz et al, 2006). The validation results suggest that incorporating the soluble C fraction into the whole continuum from solid to gaseous C is able to give a good account of the C dynamics in the early stage of decomposition. Our results showed that in all litters WOEC increased with time because (i) respiration rate decreased faster than catalysis rate (case of *Molinia* litter; $m_r > m_c$, Table 4), (ii) catalysis rate remained high throughout the time of the experiment (case of *Betula* litter; highest a_c among the three litters, Table 4, Fig 3a,). The intermediate decrease of exo-enzyme catalysis rate coupled to the high respiration rate, which decreased slowly, explains the lowest amount of WEOC in the *Betula* litters. The *Sphagnum* litter presented slightly more complicated features than the other two litters. The initial catalysis rate was high, but it decreased rapidly to a constant rate. While the catalysis rate remained constant, the respiration rate carried on decreasing. Thus, after about 15 days of incubation, the rate at which catalysis rate decreased was lower than the rate at which respiration decreased. This explains the increasing WEOC after 2 weeks of incubation (Fig. 2d). These conclusions drawn from the model are supported by the analysis of the WEOM chemical characteristics. Decrease of aromaticity coupled to increase of sugar content in WEOM suggests that exo-enzyme catalysis carry on while respiration decreased to a level where all the OM available could not be processed. As respiration could not use all the substrate available, carbon amount could increase in solution.

The sensitivity tests showed that the WEOC pool could vary dramatically when catalysis and respiration rates did not balance each other out (Fig. 4). WEOC is, quantitatively speaking, the smallest pool. A slight increase in the amount of solid mass loss (Fig. 4a) or a slight decrease of the amount of WEOC respired (Fig. 4h) generate a significant increase in W (Fig. 4de). These results suggest that the WEOC compartment is the most sensitive one to the reaction rates and as such it may be the most useful compartment to investigate when the effects of biotic or abiotic factors are

tested on these rates. These modelling results are supported by Delarue et al. (2011) who showed, *in situ*, that one of the most sensitive variables to their temperature enhancement treatment was the WEOC.

The C:N ratio of the substrate could also influence the amount and characteristics of the WEOC. The C:N ratio of the microbial biomass is lower than the substrate they live on (Francez et al, 2000). Following Schimel and Weintraub (2003) model, such situation could lead to overflow of CO_2: microbial biomass has to over consume OM with a high C:N ratio until they cover their N requirement. This overflow of CO_2 seemed not to occur as CO_2 production was the lowest in the *Sphagnum* and *Molinia* litter. Hadas et al (1998) suggested that in such situation, C that is not used could be stored in form of a polysaccharides-like pool. Instead of being stored, this C could also be excreted out of the cells. Such overflow/excretion could participate to the DOC built up and explain the soluble saccharides increase observed in our experiment. Further research is needed to confirm or infirm this mechanism.

Constant versus decreasing rates

The proposed model showed that allowing the reaction rates to decrease with time in a negative exponential fashion better described the C dynamic than setting constant rates. Running the model by allowing the decrease of one out of the two fluxes showed that it did not improved much the description of experimental results (Table 3). All rates calculated tended to decrease. This suggests that during the early decomposition stage, all these rates may have been constrained in one way or another. Our present work supports the generalized decomposition models proposed by Rovira and Rovira (2010), highlighting that, under optimal environmental conditions, the decrease of process rates with time, rather than constant rates, is a common feature of C litter dynamics.

Bowen et al (2009) showed that DOC mineralisation kinetics follows a double exponential first order model (constant rate of soluble labile and recalcitrant pool decomposition). The negative exponential decrease of respiration rate may result from a shift in the quality of the available substrate, from labile compounds at the beginning to recalcitrant ones afterwards. However, $SUVA_{280}$ results suggest that recalcitrant DOC such as aromatic compounds did not increase in the course of the experiment. Furthermore, the analysis of carbohydrate monomers showed that glucose, whose degradation is the main energy provider for living cells, was present in the WEOC and thus readily available at all times. Such saccharides are present because of exo-enzymes catalysis. This results show that studying the decomposition rate of the DOC in isolation from the pool it originates from could not give pertinent

insights into the DOC dynamics in soil. Also, in early stage of the decomposition process, C substrate quality and quantity may not limit the microbial respiration rate. Other constraining variables than C substrate availability and quality may explain the exponential decrease of this rate. Among them, N availability deserves particular scrutiny. Although only three litters were tested in our work, it was observed that the slowest rates were calculated for the two litters with the highest C:N ratio (Table 1, Gogo et al, 2011). Microbial biomass can decrease as the C:N ratio of the substrate increase (Schimel and Weintraub, 2003). Thus, microbial biomasses in *Sphagnum* and *Molinia* are probably lower and much more N limited than in Betula litter. This may explain lower and more rapidly decreasing reaction rates in the two former litters.

1 pool versus 2 pools

Two pools models were implemented to determine whether the experimental results observations could be better explained by one litter pool with a decreasing rate or by two litter pools with constant catalysis rate.

Recalcitrant and labile are relative terms. Here, labile compounds were defined as non structural compounds originating from cell contents and experimentally measured as the proportion of hydrocarbons pyrolysed at 200°C. Such a labile pool was not observed in *Molinia* litter. *Molinia caerulea* is a very effective graminoid in recycling and storing its nutrients, along with an energy source in the form of starch (Taylor et al., 2001). The lack of a labile pool, as defined above, probably originates from the translocation of C compounds in storage tissue of the plant.

A labile pool was measured in the other two litters: *Sphagnum* and *Betula*. For *Betula*, the 2-pool model did not improve the goodness of fit of any variables (Table 3). In the *Sphagnum* litter, the 2-pool model slightly improved the goodness of fit of L and G, but at the expense of (i) dramatically decrase the goodness of fit of W (table 3), and (ii) increasing the number of model parameters. Furthermore, the overall goodness of fit was not improved (Table 3). Thus, using two pools with constant rate was not efficient in improving the description of our results. This suggests that either the L compartments are composed of many C pools that decompose at different constant rates This is supported by the efficient modeling properties of infinite pools techniques (Vähätalo et al., 2010).

These results also suggest that, although parsimonious models do not account for the complexity of a system, they still perform very well and deserve to be developed (Perrin et al, 2001; Rovira and Rovira, 2010). Thus, in the case of the three litters used in this study, using 2 pools is not necessary to

give a good account of the overall early C dynamics of the litter. However, our model should be tested with more recalcitrant *Sphagnum* litter such as *S. magellanicum* and *S. fuscum*.

Conclusion

The originality of the model presented here is that it takes into account simultaneously the three forms of C (solid, soluble and gaseous). This study has shown that our simple model is efficient in describing and predicting the early C dynamics of peatland litters. The OM dynamics is better described by using a single pool of solid OM, whose decomposition rate decreases with time and respiration rate that can also decrease with time. It was also shown that the soluble pool is the most sensitive one and more attention should be paid to this pool. However, it should not be considered in isolation, but in permanent relation with its source (solid OM) and sink (gaseous C) pools. Our model characteristics enable the assessment of the actual rate of enzymatic catalysis, which is not possible with specific enzymatic assays on an artificial substrate. Furthermore it is easy to implement experimentally.

As our model performed well, it can be used in studying differences of C dynamics in the most important functional groups present in peatlands: bryophytes, graminoids and trees. This is particularly important in the actual context of vegetation change caused by human disturbances, and area of study that still need to be developed (Limpens et al., 2008).

Acknowledgement

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Table captions

Table 1. Elemental composition of the *Sphagnum*, *Betula* and *Molinia* litters at the beginning of the experiment (n=3; values in parenthesis are 1 s.e.).

Table 2. Average (±1 s.e.) mass remaining after 46 days, Water Extractable Organic Carbon (WEOC), CO_2 production and Specific Ultra-Violet Absorption at 280 nm ($SUVA_{280}$). Different letters show significant differences ($P < 0.05$)

Table 3. Relative mean square error (RMSE) estimated for models using one or two pools (1 or 2) and all constant (C), either constant or negative exponentially decreasing rates (C + Ne), or all negative exponentially decreasing rates (Ne + Ne). Number in parenthesis is the number of parameters used in each model, number in italic are the best fit for each variable and number in bold is the overall best fit.

Table 4. Parameters estimated with the model that gives the best fit (1cNE+rNE), with m_c, a_c, and b_c the model parameters for the exo-enzymes catalysis rate and m_r, a_r, and b_r. the model parameters for respiration rate (m = rates at which each rate decrease, a+b = initial rates, a = final rate, Rovira and Rovira, 2010).

Table 5. Kinetics of the mono- and total saccharides expressed as the proportion to initial dry matter content (µg g^{-1} initial mass of dry mass)

Figure captions

Figure 1. Structure of the litter C mass flow model composed of three compartments corresponding to the solid, aqueous and gaseous forms of C: the Litter (L), the Water Extractable Organic Carbon (WEOC; W) and the cumulative C-CO_2 respired (G), respectively. The 1-pool model is composed of only one pool of C (a) and the 2-pool model is composed of two pools of C (b), with a more labile one (LL) and a more recalcitrant one (LR). Solid lines indicate the rates of catalysis and respiration. The L pool flows into the WEOC at the catalysis rates c (1 pool) and c1 and c2 (2 pools). The WEOC is respired at the rate r.

Figure 2. Measured (diamond, square and triangle) and modelled (lines) kinetics of the litter C-mass remaining (L: abc), WEOC (W: def) and cumulative CO_2-C (G: ghi) in the *Sphagnum* (grey diamond), *Betula* (white square) and *Molinia* (black triangle) litters. The model used was the 1cNe+rNe (the model giving the overall best fit).

Figure 3. Modelled kinetics of the catalysis c (a) and respiration r (b) rates from the 1cNe+rNe model.

Figure 4. Sensitivity of the model when catalysis (adg) or respiration (beh) parameters and both (cfi) are tuned to maximise (dark: + 10% change, and light: + 50% change, grey unbroken lines) or minimize (dark: - 10% change, and light: - 50% change, grey dashed lines) fluxes from a reference (blue line).

Figure 5. Prediction of mixed *Sphagnum* + *Betula* (adg), *Sphagnum* + *Molinia* (beh) and *Betula* + *Molinia* (cfi) litter C dynamics calculated with parameters obtained with the calibration.

Figure 6. Kinetics of the aromaticity (SUVA 280) of the soluble OM extracted from the *Sphagnum* (green diamond), *Betula* (red square) and *Molinia* (blue triangle) litters (n = 2, ±1s.e.).

Tables

Table 1.

	C		N		H		C:N		H:C	
Sphagnum cuspidatum	434	(1)	6.12	(0.06)	59.0	(0.3)	82.7	(0.61)	1.63	(0.01)
Betula spp	522	(2)	13.0	(0.27)	62.1	(0.2)	46.8	(0.9)	1.43	(0.02)
Molinia caerulea	482	(6)	5.95	(0.23)	62.1	(0.2)	94.7	(2.79)	1.54	(0.01)

Table 2.

	Sphagnum cuspidatum	*Betula* spp	*Molinia caerulea*
Dry mass remaining after 46 days (% original dry mass, ± 1 s.e., n = 3)	79.4 (± 3.15)^{ab}	75.7 (± 2.75)^{a}	90.0 (± 1.07)^{b}
Water Extractable Organic Carbon (mg C g^{-1} dry mass, ± 1 s.e., n = 14)	3.07 (± 0.31)^{a}	1.45 (± 0.25)^{b}	3.05 (± 0.52)^{a}
CO_2 production (in µg C-CO_2 g^{-1} dry mass h^{-1}, ± 1 s.e., n = 12)	167 (± 58.3)^{ab}	302 (± 34.5)^{a}	116 (± 20.0)^{b}
$SUVA_{280}$ (l mg^{-1} C cm^{-1}, ± 1 s.e., n = 14)	0.009 (± 0.001)^{a}	0.017 (± 0.002)^{b}	0.024 (± 0.003)^{c}

Table 3.

Litters	Variables	Model 1 Pool				Model 2 Pools	
		1C (2)	1cNe+rC (4)	1cC+rNe (4)	1cNe+rNe (6)	2C (6)	2cC+rNe (7)
	L	0.54	0.31	0.53	0.26	*0.18*	0.50
Sphagnum	W	30.5	30.3	18.6	*4.19*	29.3	18.49
	G	13.9	7.2	12.4	5.3	*3.91*	11.79
	sum	44.9	37.8	31.5	**9.8**	33.4	30.79
	L	0.36	0.36	0.36	*0.22*	0.26	0.36
Betula	W	37.8	37.8	21.4	*18.6*	37.2	21.4
	G	4.97	4.97	4.55	*2.84*	3.2	4.5
	sum	43.10	43.10	26.33	**21.71**	40.7	26.3
	L	0.40	0.40	0.37	*0.23*	-	-
Molinia	W	47.0	47.0	25.1	*14.5*	-	-
	G	13.0	13.0	10.3	*3.57*	-	-
	sum	60.4	60.4	35.7	**18.32**		

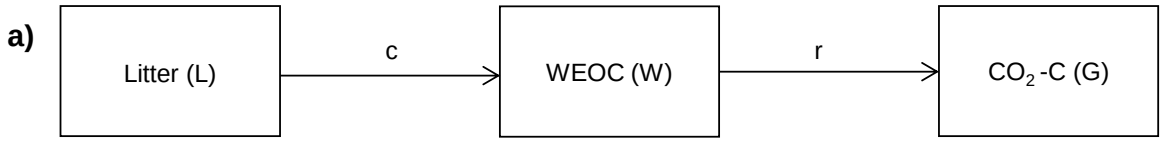
Table 4.

Parameters	*Sphagnum cuspidatum*	*Betula spp*	*Molinia caerulea*
m_c	0.23	0.047	0.014
a_c	0.0019	0.0033	0.0008
b_c	0.0031	0.0014	0.0019
m_r	0.036	0.028	0.043
a_r	0.074	0	0
b_r	0.72	2.70	0.92

Table 5.

	Days	2	6	13	20	27	34
Sphagnum cuspidatum	Fructose	1984	15.2	3.54	0	0	0
	Glucose	8.30	3.59	4.30	5.22	95	30.8
	Glycerol	17.5	9.2	13.2	11.6	19.5	26.5
	Sorbitol	0.49	0.37	*	*	4.33	17.1
	All sugars	**2019**	**40.2**	**23.2**	**31.1**	**301**	**119**
Betula spp							
	Fructose	15.0	1.26	6.69	0	0	0
	Glucose	2.31	5.38	7.51	4.26	6.99	5.68
	Glycerol	29.6	7.26	12.4	7.91	21.4	15.6
	Sorbitol	0	0	0	0	4.16	4.92
Molinia caerulea	**All sugars**	**47.5**	**16.3**	**36.4**	**25.7**	**53.9**	**59.2**
	Fructose	2.00	6.30	11.6	0.75	2.31	0
	Glucose	3.76	33.7	17.5	4.54	37.7	32.5
	Glycerol	60.7	12.9	14.6	9.9	25.0	26.1
	Sorbitol	0	0	0.14	0	5.84	12.9
	All sugars	**75.3**	**87.6**	**60.1**	**30.2**	**108**	**147**

Figures

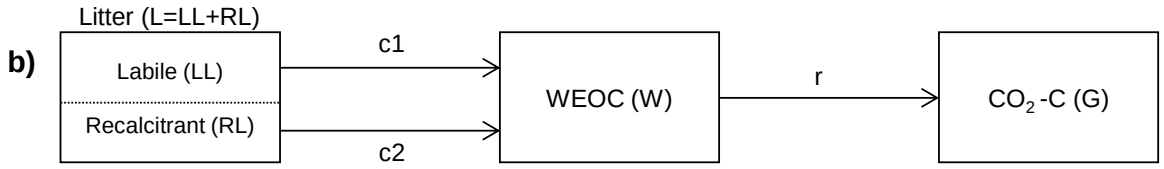


1C: **1** pool of OM in L with **C**onstant fluxes

1cNe+rC: **1** pool with **c** decreasing (**N**egative **e**xponential decrease) + **r** **C**onstant

1cC+rNe: **1** pool with **c** **C**onstant + **r** **Ne** decreasing

1cNe+rNe: **1** pool with **c** **Ne** decreasing + **r** **Ne** decreasing



2C: **2** pools of OM in L (LL and RL) + **C**onstant fluxes

2cC+rNe: **2** pools with **c**1 and c2 **C**onstant + **r** **Ne** decreasing)

L: litter
LL: more labile litter
RL: more recalcitrant litter
WEOC: Water Extractable Organic Carbon
c: decomposition through exo-enzymes catalysis
r: respiration

Fig. 1.

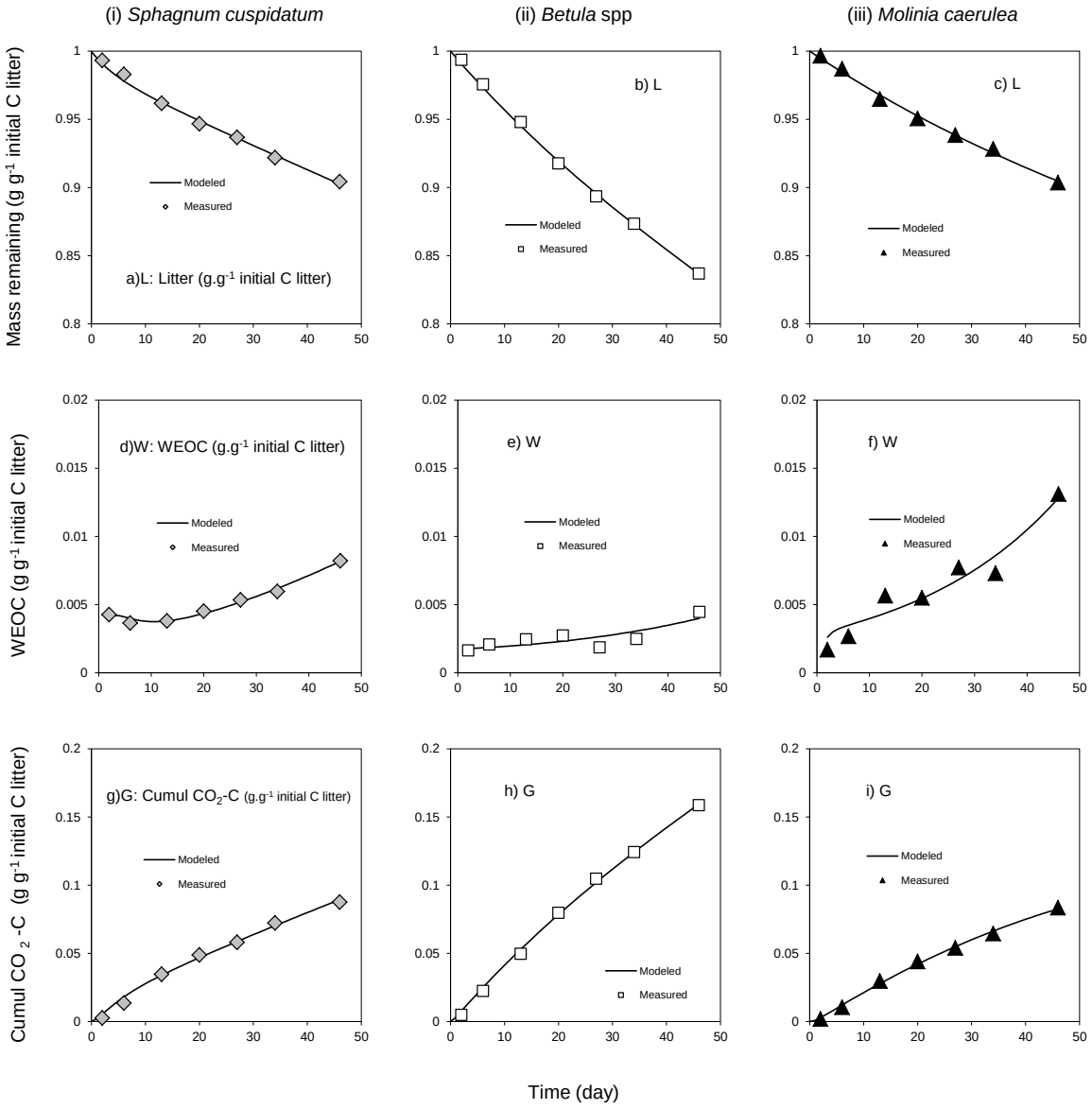

(i) Sphagnum cuspidatum
(ii) Betula spp
(iii) Molinia caerulea
Mass remaining (g g-1 initial C litter)
a)L: Litter (g.g-1 initial C litter)
b) L
c) L
Modeled
Measured
WEOC (g g-1 initial C litter)
d)W: WEOC (g.g-1 initial C litter)
e) W
f) W
Cumul CO 2 -C (g g-1 initial C litter)
g)G: Cumul CO2-C (g.g-1 initial C litter)
h) G
i) G
Time (day)

Fig. 2.

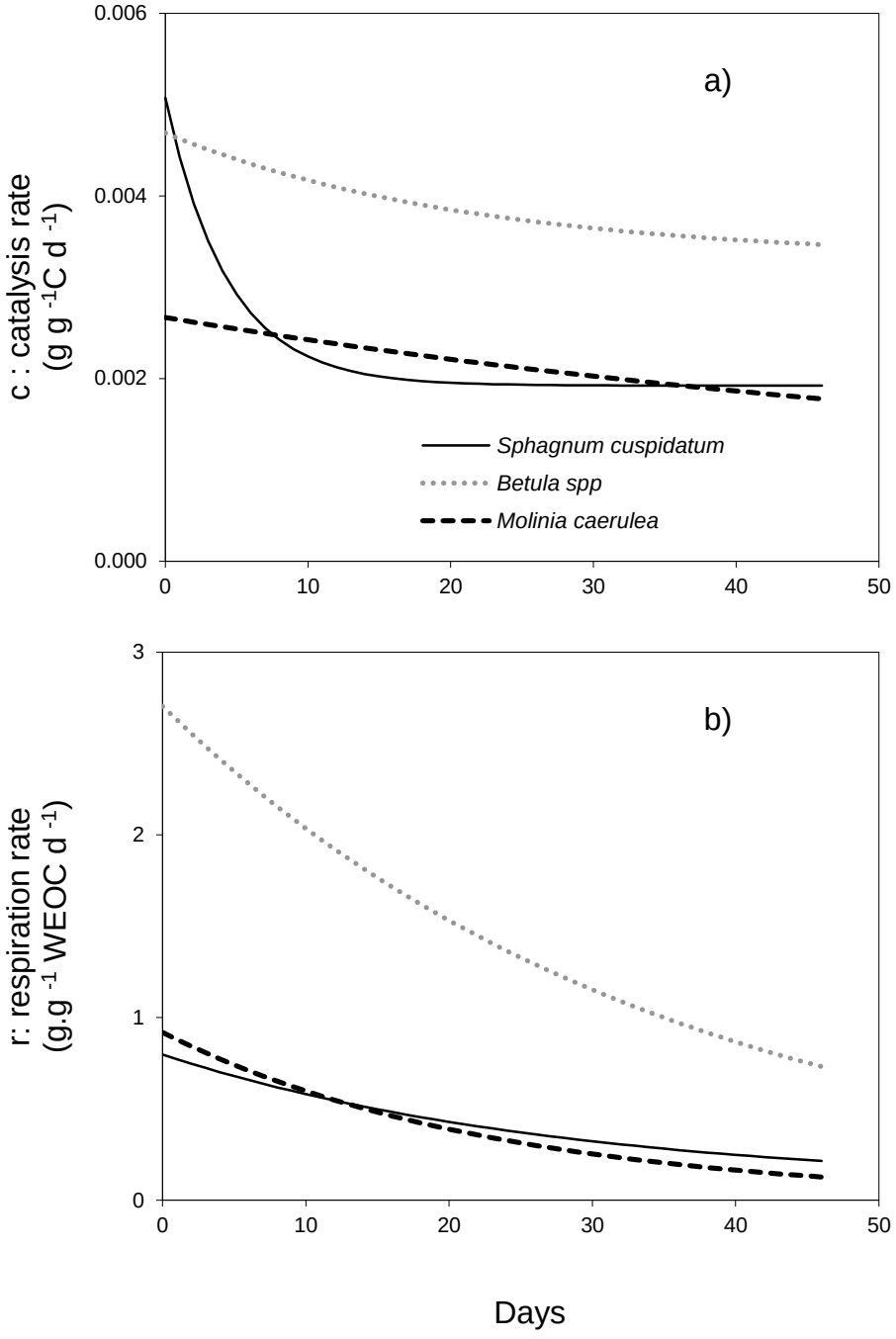

a)
b)
c : catalysis rate
(g g -1C d -1)
r: respiration rate
(g.g -1 WEOC d -1)
Sphagnum cuspidatum
Betula spp
Molinia caerulea
0.006
0.004
0.002
0.000
3
2
1
0
0
10
20
30
40
50
Days

Fig. 3.

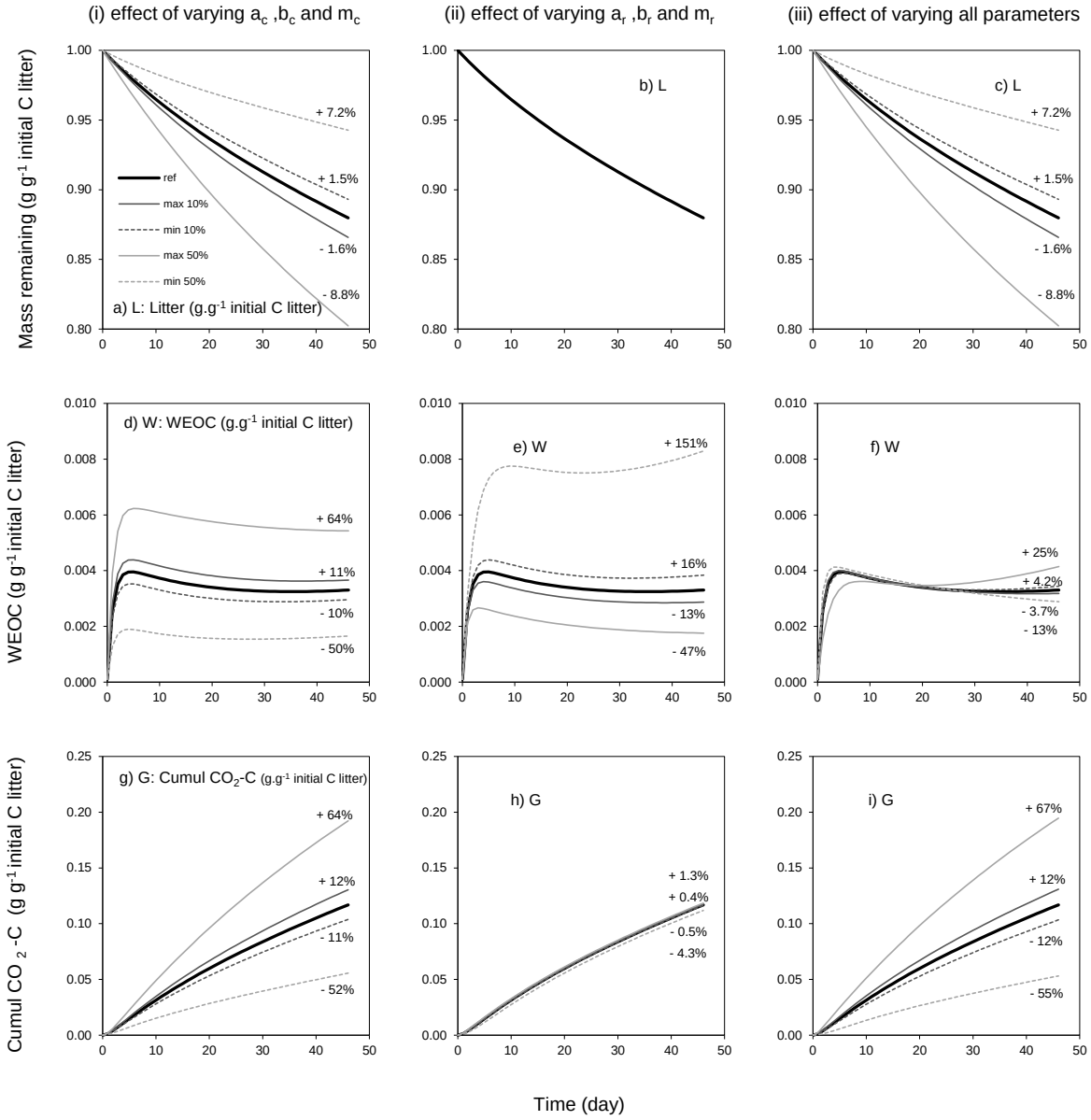

(i) effect of varying a_c ,b_c and m_c
(ii) effect of varying a_r ,b_r and m_r
(iii) effect of varying all parameters
Mass remaining (g g-1 initial C litter)
WEOC (g g-1 initial C litter)
Cumul CO 2 -C (g g-1 initial C litter)
Time (day)
a) L: Litter (g.g-1 initial C litter)
b) L
c) L
d) W: WEOC (g.g-1 initial C litter)
e) W
f) W
g) G: Cumul CO2-C (g.g-1 initial C litter)
h) G
i) G
ref
max 10%
min 10%
max 50%
min 50%
+ 7.2%
+ 1.5%
- 1.6%
- 8.8%
+ 64%
+ 11%
- 10%
- 50%
+ 151%
+ 16%
- 13%
- 47%
+ 25%
+ 4.2%
- 3.7%
- 13%
+ 64%
+ 12%
- 11%
- 52%
+ 1.3%
+ 0.4%
- 0.5%
- 4.3%
+ 67%
+ 12%
- 12%
- 55%

Figure 4.

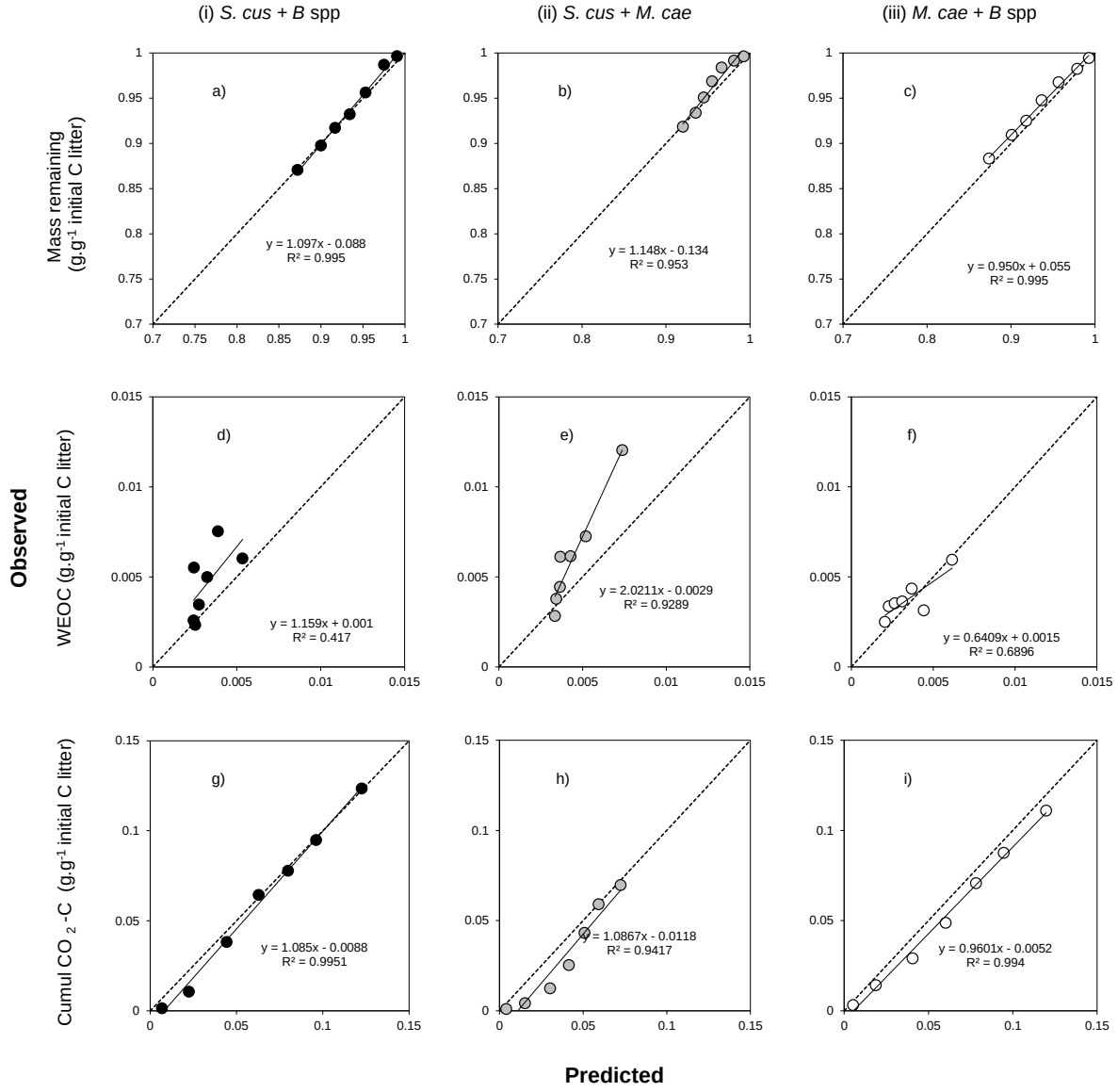

(i) S. cus + B spp
(ii) S. cus + M. cae
(iii) M. cae + B spp
Mass remaining (g.g-1 initial C litter)
WEOC (g.g-1 initial C litter)
Cumul CO2-C (g.g-1 initial C litter)
Observed
Predicted
a)
y = 1.097x - 0.088
R² = 0.995
b)
y = 1.148x - 0.134
R² = 0.953
c)
y = 0.950x + 0.055
R² = 0.995
d)
y = 1.159x + 0.001
R² = 0.417
e)
y = 2.0211x - 0.0029
R² = 0.9289
f)
y = 0.6409x + 0.0015
R² = 0.6896
g)
y = 1.085x - 0.0088
R² = 0.9951
h)
= 1.0867x - 0.0118
R² = 0.9417
i)
y = 0.9601x - 0.0052
R² = 0.994

Fig. 5.

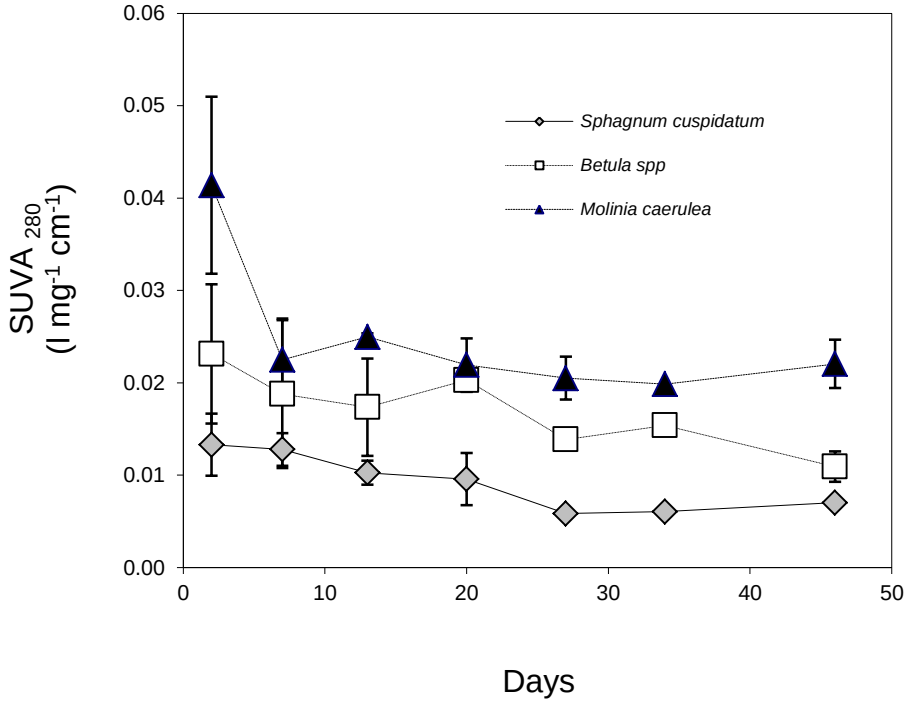

0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
40
50
SUVA 280
(l mg-1 cm-1)
Sphagnum cuspidatum
Betula spp
Molinia caerulea
Days

Fig. 6.