

Stoichiometric controls on carbon, nitrogen, and phosphorus dynamics in decomposing litter

STEFANO MANZONI,¹ JOHN A. TROFYMOW,² ROBERT B. JACKSON,³ AND AMILCARE PORPORATO^{1,4}

¹*Civil and Environmental Engineering Department, Duke University, 121 Hudson Hall, Box 90287, Durham, North Carolina 27708-0287 USA*

²*Canadian Forest Service, Pacific Forestry Centre, 506 West Burnside Road, Victoria, British Columbia V8Z 1M5 Canada*

³*Department of Biology and Nicholas School of the Environment, Duke University, Box 90338, 3311 FFSC, Durham, North Carolina 27708 USA*

Abstract. The mineralization of nitrogen and phosphorus from plant residues provides an important input of inorganic nutrients to the soil, which can be taken up by plants. The dynamics of nutrient mineralization or immobilization during decomposition are controlled by different biological and physical factors. Decomposers sequester carbon and nutrients from organic substrates and exchange inorganic nutrients with the environment to maintain their stoichiometric balance. Additionally, physical losses of organic compounds from leaching and other processes may alter the nutrient content of litter. In this work, we extend a stoichiometric model of litter nitrogen mineralization to include (1) phosphorus mineralization, (2) physical losses of organic nutrients, and (3) chemical heterogeneity of litter substrates. The enhanced model provides analytical mineralization curves for nitrogen and phosphorus as well as critical litter carbon:nutrient ratios (the carbon:nutrient ratios below which net nutrient release occurs) as a function of the elemental composition of the decomposers, their carbon-use efficiency, and the rate of physical loss of organic compounds. The model is used to infer the critical litter carbon:nutrient ratios from observed nitrogen and phosphorus dynamics in about 2600 litterbag samplings from 21 decomposition data sets spanning arctic to tropical ecosystems. At the beginning of decomposition, nitrogen and phosphorus tend to be immobilized in boreal and temperate climates (i.e., both C:N and C:P critical ratios are lower than the initial ratios), while in tropical areas nitrogen is generally released and phosphorus may be either immobilized or released, regardless of the typically low phosphorus concentrations. The critical carbon:nutrient ratios we observed were found to increase with initial litter carbon:nutrient ratios, indicating that decomposers adapt to low-nutrient conditions by reducing their carbon-use efficiency. This stoichiometric control on nutrient dynamics appears ubiquitous across climatic regions and ecosystems, although other biological and physical processes also play important roles in litter decomposition. In tropical humid conditions, we found high critical C:P ratios likely due to high leaching and low decomposer phosphorus concentrations. In general, the compound effects of stoichiometric constraints and physical losses explain most of the variability in critical carbon:nutrient ratios and dynamics of nutrient immobilization and release at the global scale.

Key words: carbon; decomposer stoichiometry; microbial immobilization; mineralization; nitrogen; nutrient cycling; phosphorus; plant residue decomposition.

INTRODUCTION

Nitrogen and phosphorus are considered the most important limiting elements for vegetation in terrestrial ecosystems (Vitousek 1984, Chapin et al. 1986, Vitousek and Howarth 1991). The amount of plant-available nitrogen and phosphorus constrains both natural and managed ecosystems, including agricultural productivity where fertilizers are not used (Seneviratne 2000). At decadal and longer time scales typical of ecosystem development, the predominant source of phosphorus is from rock weathering, while nitrogen is of atmospheric

origin. Accordingly, plants growing on young soils tend to be nitrogen limited, while vegetation on older, highly weathered soils is often phosphorus limited (Vitousek 1984, Jobbagy and Jackson 2001, Reich and Oleksyn 2004). Similarly, peatland soils may have large phosphorus stocks bound in resistant organic forms that are not readily available for plant use. These broad-scale trends in soil features, coupled with smaller scale heterogeneity in soil-vegetation interactions, produce a spectrum of nutrient availabilities and patterns of nutrient limitation, which in turn result in plant tissues and residues with very different chemical compositions (Vitousek and Howarth 1991, McGroddy et al. 2004, Reich and Oleksyn 2004, Townsend et al. 2007). At the yearly time scale, much of the available inorganic

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⁴ Corresponding author. E-mail: amilcare@duke.edu

nutrient comes from biological mineralization of plant residues. Thus, it is important to quantify nutrient interactions and patterns of release from chemically different litter types and under different climatic conditions.

Nutrient mineralization from plant residues is predominantly controlled by the activity of decomposer organisms. Decomposers tend to grow following relatively rigid stoichiometric requirements (Cleveland and Liptzin 2007), and carbon and nutrients are typically processed together in order to achieve balanced growth conditions (Sinsabaugh and Moorhead 1994, Sinsabaugh et al. 2008). Since nitrogen and phosphorus concentrations in plant litter tend to be low compared to the decomposer requirements, nutrients may be initially immobilized from the environment by decomposers until the nutrient concentrations in the litter reach a critical value and net release occurs (Aber et al. 1978, Berg and McLaugherty 2003, Moore et al. 2006, Parton et al. 2007). As a consequence of this coupling between carbon and nutrients through decomposer activity, a linear increase in litter nitrogen or phosphorus concentrations as a function of the remaining carbon in litter has been observed (Waksman 1924, Gosz et al. 1973, Aber and Melillo 1980). Under most conditions, physical processes such as leaching also play a role in the early phases of decomposition, although in humid environments they may be important through all phases of decomposition, when water flushes away soluble organic compounds, or freeze–thaw cycles mechanically disrupt residue texture, causing losses by fragmentation (Yavitt and Fahey 1986, Currie and Aber 1997, Berg and McLaugherty 2003, Cleveland et al. 2006).

Although simultaneous patterns of nitrogen and phosphorus immobilization and release have been documented in the field, mechanistic models have typically focused on nitrogen alone (Manzoni et al. 2008a, Manzoni and Porporato 2009). Among the few models that include phosphorus cycling, only one has been specifically applied to nitrogen and phosphorus dynamics in different litter types under natural conditions (Bosatta and Ågren 1991, Hyvonen et al. 2000). Importantly, very few models account for physical losses of organic substrates during decomposition (e.g., Currie and Aber 1997, Michalzik et al. 2003), neglecting a potentially important factor in the litter nutrient balance, especially for nutrients in organic form that are prone to leaching such as phosphorus. A mechanistic representation of nutrient dynamics and interactions in decomposing litter is therefore needed that includes both biological and physical factors. Such a model may be useful to analyze the variety of observed patterns arising from chemically different litter types and under different environmental conditions.

Here we extend the framework and model of Manzoni et al. (2008a) to describe litter carbon, nitrogen, and phosphorus dynamics, with the aim of explaining the patterns of nutrient immobilization and release that

have been observed across ecosystems worldwide. We use 21 terrestrial decomposition data sets, including the extensive Canadian Intersite Decomposition Experiment (CIDET; Trofymow and CIDET Working Group 1998), and several wood decomposition chronosequences (Table 1). We derive critical carbon:nutrient ratios (below which net nutrient release occurs) in terms of decomposer characteristics, including carbon-use efficiency and elemental composition, as well as specific litter and environmental parameters. Because the decomposer C:N ratio is relatively constant across substrate types, Manzoni et al. (2008a) have shown that the variability of the critical C:N of the litter is largely explained by a reduced decomposers' carbon-use efficiency with decreasing initial litter nitrogen concentration. This response to low organic nitrogen availability is common to bacteria and consumers at higher trophic levels (Mattson 1980, Pandian and Marian 1986, Russell and Cook 1995, del Giorgio and Cole 1998, Elser et al. 2000). Similarly, reduced efficiency would be expected also under conditions of low organic phosphorus availability (Elser et al. 2000, Sterner and Elser 2002), but this hypothesis has not, to our knowledge, been tested for terrestrial decomposer organisms.

Based on this theoretical framework, we analyze the patterns of immobilization and mineralization of both nitrogen and phosphorus, assessing the effects of both nutrients on the biochemical characteristics of the decomposer communities. We then compute the critical carbon:nutrient ratios as a function of these characteristics and analyze their patterns of variation across litter types and climatic conditions. As a result, we obtain simple relationships between the thresholds of net nutrient release and litter type that are valid at the global scale.

METHODS

Data description

Using data from the Canadian Intersite Decomposition Experiment (CIDET) and 20 other literature sources, we compiled a database of litter carbon, nitrogen, and phosphorus contents during decomposition (Table 1). Each decomposition data set was associated with a broad climatic region according to the mean annual temperature. We distinguished among arctic and boreal, temperate, and tropical regions. The CIDET data set encompasses ten types of leaf litter decomposed at 21 locations in Canada (Trofymow and CIDET Working Group 1998, Trofymow et al. 2002, Moore et al. 2006). The other decomposition data sets are mainly from boreal and temperate forest ecosystems but also include tropical regions (Table 1). Except for two data sets based on a reciprocal litterbag design (CIDET; and Thompson and Vitousek 1997), all the other studies focus on decomposition of local litter material.

In this paper our focus is on surface litter decomposition in terrestrial ecosystems, where external inputs of

TABLE 1. Data set description.

Data set	Method†	Litter type‡	Climatic region§	(C/N) _{L,0} range	(C/P) _{L,0} range
Lambert et al. (1980)	CS	□	BR	332	3992
Foster and Lang (1982)	CS	□	BR	624–714	5000–8568
Edmonds (1987)	LB	□	TM	118–209	866–1151
Sollins et al. (1987)	CS	□	TM	454–625	5387–12 407
Blair (1988)	LB	◇	TM	56–86	525–1137
Berg and McClaugherty (1989)	LB	◇, △	BR, TM	16–147	208–2632
Means et al. (1992)	CS	□	TM	620	23 682
Tripathi and Singh (1992)	LB	○, ◇, □	TR	37–59	590–1842
Busse (1994)	CS	□	TM	1327	14 959
Zhu and Ehrenfeld (1996)	LB	△	TM	58	873
Thompson and Vitousek (1997)	LB	◇	TR	31–40	357–455
Trofymow and CIDET Working Group (1998)	LB	○, ◇, △	BR, TM	39–82	369–2122
Krankina et al. (1999)	CS	□	BR	277–294	7056–13 573
Liu et al. (2000)	LB	○, ◇	TM	32–39	415–708
Chuyong et al. (2002)	LB	◇	TR	28–49	515–1282
Hirobe et al. (2004)	LB	◇	TR	33–73	1419–11 450
Osono and Takeda (2004, 2005)	LB	◇, △	TM	17–94	352–2500
Isaac and Nair (2005)	LB	◇	TR	33–47	331–1470
Xu (2006)	LB	△	TR	59–79	2165–3615
Li et al. (2007)	LB	◇, △	TM	30–70	381–849
Ball et al. (2009)	LB	◇	TM	40–87.3	1001–2444

† Key to abbreviations: LB, litterbag method; CS, chronosequence study.

‡ Key to symbols: ○, grass leaves and moss; ◇, broadleaved tree and shrub leaves; △, conifer needles; □, woody residues.

§ Key to abbreviations: BR, polar, subpolar, and boreal (open black symbols in Figs. 3, 7, and 8); TM, temperate (solid gray symbols); TR, tropical and subtropical (open gray symbols).

organic carbon and nutrients in the litterbag are generally negligible. Hence, no data from litterbags buried into the soil or decomposed in wetland sites were included here. We also excluded litter fertilization studies where the availability of inorganic nutrients is significantly larger than in natural conditions. To have time series of carbon and nutrient contents representative of the entire decomposition process, we only selected those data sets presenting both significant mass losses (generally >50%) and at least seven data points. We treated observations from the same litter type decomposed at different sites within a given climatic region as a single data set, on the grounds that site effects should be generally less important than stoichiometric effects (Parton et al. 2007).

We also added six chronosequence studies of coarse wood decomposition to widen the range of initial C:N and C:P ratios (Table 1). Only a few points were generally available in these data sets (four to seven observations), but they generally covered several decades of decomposition, better characterizing the later stages of degradation. The temporal evolution of wood density was used as a proxy for the wood dry mass (or carbon mass) evolution in some of the data sets where no other specific information was given (Foster and Lang 1982, Sollins et al. 1987, Means et al. 1992, Busse 1994). Although this approximation might tend to overestimate nutrient immobilization in decomposing logs (Krankina et al. 1999), the uncertainties in the mass (and hence carbon) temporal evolution are not expected to significantly affect patterns of accumulation and release for nitrogen and phosphorus in these nutrient-poor substrates. For all data sets, a carbon concentra-

tion of 50% was assumed unless specific information was available.

Mineralization and balance equations

Nitrogen and phosphorus release curves can be obtained analytically using a simplified lumped model of litter dynamics valid at monthly to yearly time scales (depending on the climatic conditions that dictate the overall decomposition rates). Using a similar approach as Manzoni et al. (2008a), we consider the total mass of carbon C_L and total mass of a nutrient element E_L in a litterbag or in a given volume of decomposing wood, where the element E may be nitrogen or phosphorus (Fig. 1). The decomposition flux, controlled by substrate and decomposer availability as well as environmental conditions, is denoted by D . Climatic effects and availability of nutrients in the environment are accounted for in the functional dependence of D on litter moisture, temperature, and inorganic nitrogen and phosphorus. These effects, as will be made clear below, only change the reaction rate, but not the carbon–nutrient relationship in decomposing litter. We model two biological fluxes involved in the decay process and related to the flux D : heterotrophic respiration, by which organic carbon is mineralized and released to the atmosphere, and net nutrient mineralization, which controls the release and accumulation of nutrients in the residues. We also explicitly consider physical losses (mainly leaching) of organic compounds from the litter (Fig. 1).

Leaching of organic nutrients from litter typically takes place in two phases. One is an initial, very rapid phase where leaching of soluble compounds is brought about by some intense rainfall event or freeze–thaw cycle (Gosz et al. 1973, Aber and Melillo 1980, Yavitt and

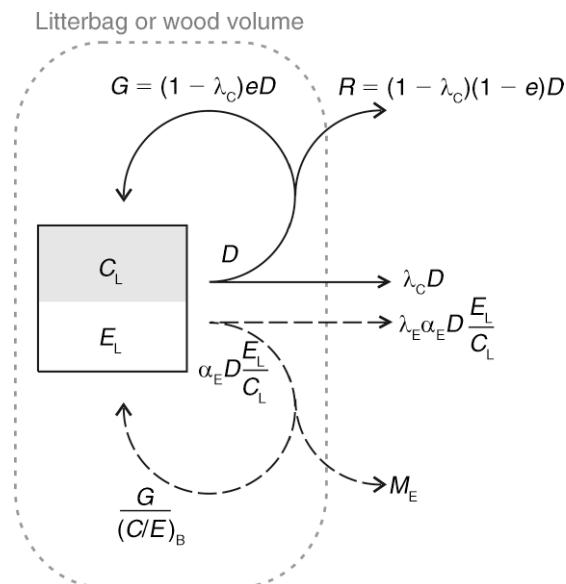


FIG. 1. Schematic representation of litter carbon (C_L) and nutrient (E_L , representing either litter N or litter P) dynamics. Solid lines represent the carbon fluxes (D , decomposition flux; G , growth rate; e , carbon use efficiency; R , respiration rate; λ_C , fraction of D lost through leaching), and dashed lines represent the nutrient fluxes (M_E , net nutrient mineralization flux; α_E , coefficient accounting for preferential decomposition of E_L ; λ_E , fraction of nutrient decomposition lost through leaching; $(C/E)_B$, decomposer C/E ratio). Note that M_E is defined to be positive when nutrient is released from the litter and negative when immobilization occurs.

Fahey 1986). The other is a less intense but prolonged phase when compounds solubilized by extracellular enzymes and freeze–thaw cycles or small litter fragments are lost from the litterbags (Currie and Aber 1997). For longer timescales (e.g., years) the initial loss is effectively an instantaneous process, so we assume that the early leaching event is equivalent to changing the initial condition of the litter (Aber and Melillo 1980, Berg and Staaf 1987). The degree of this correction is computed from the observed nutrient losses during the early phase of decomposition (see *Methods: Data analysis*). To model leaching during the following phases of decomposition, we assume that constant fractions of carbon and nutrient fluxes from residue decomposition are lost from the system (coefficients λ_C and λ_E ; see Fig. 1).

The remaining carbon from decomposition is either converted to new decomposer biomass according to a carbon-use efficiency e (the fraction $(1 - \lambda_C)e$) or respired (the fraction $(1 - \lambda_C)(1 - e)$; see Fig. 1). Since decomposers grow at a rate $G = (1 - \lambda_C)eD$ in terms of carbon mass, they also need to assimilate proportional amounts of nutrient E to maintain their given C/E ratio, as indicated by $(C/E)_B$. Both the parameters e and $(C/E)_B$ are assumed to be constant through time.

The stoichiometric flux of organic nutrients mobilized from a perfectly homogeneous litter is $D(E_L/C_L)$ (Fig. 1). To account for the chemical heterogeneity of the

residues in a simplified way, we use a coefficient α_E that modifies the flux $D(E_L/C_L)$. When α_E is larger than one, decomposers preferentially assimilate nutrient-rich compounds from the litter residues, resulting in slower decomposition in nutrient-poor substrates. The theoretical nutrient mineralization fluxes M_E can be computed as the difference between the assimilated nutrients (i.e., $(1 - \lambda_E)\alpha_E D(E_L/C_L)$) and the stoichiometric demand (i.e., $G(C/E)_B^{-1}$):

$$M_E = D \left[\frac{(1 - \lambda_E)\alpha_E E_L}{C_L} - \frac{(1 - \lambda_C)e}{(C/E)_B} \right]. \quad (1)$$

When M_E is positive, the excess organic nutrients that are assimilated are mineralized; if M_E is negative, then nutrient demands are met by nutrient immobilization. The mass balance equations for C_L and E_L in a litter cohort can be written as

$$\frac{dC_L}{dt} = -D[(1 - \lambda_C)(1 - e) + \lambda_C] \quad (2)$$

and

$$\frac{dE_L}{dt} = -M_E - \lambda_E \alpha_E D \frac{E_L}{C_L} = -\alpha_E D \left[\frac{E_L}{C_L} - \frac{1}{(C/E)_{CR}} \right] \quad (3)$$

where $(C/E)_{CR}$ is a generalized critical carbon : nutrient ratio that also accounts for physical losses of organic carbon (controlled by the parameter λ_C), and preferential assimilation of nutrient-rich compounds (α_E):

$$(C/E)_{CR} = \frac{\alpha_E (C/E)_B}{(1 - \lambda_C)e}. \quad (4)$$

When the ratio C_L/E_L is larger than the critical ratio, immobilization of the nutrient from the inorganic pool is needed; otherwise net nutrient mineralization occurs. In most litter types, as shown below, the initial litter carbon : nutrient ratio is higher than $(C/E)_{CR}$, resulting in an early immobilization phase during which C_L/E_L decreases, followed by a net release phase when $C_L/E_L < (C/E)_{CR}$. In Eq. 4, high leaching rates λ_C and high values of α_E lead to higher values of $(C/E)_{CR}$. When no leaching occurs (i.e., $\lambda_C = \lambda_E = 0$), and carbon and E are decomposed in proportion equal to their ratio (i.e., $\alpha_E = 1$), $(C/E)_{CR} = (C/E)_B/e$, which is the typical definition based solely on decomposer characteristics (Bosatta and Staaf 1982, Manzoni and Porporato 2007). Note that Eq. 3 does not depend on λ_E because the mineralization flux M_E compensates any leaching losses of nutrients in organic form by increasing immobilization.

Nutrient release curves

Proceeding as in Manzoni et al. (2008a), we combine Eqs. 2 and 3, eliminating the direct time dependence (with the associated effects of climatic parameters and external nutrient availability), and obtain a single first-order ordinary differential equation for the independent variable C_L and the dependent variable E_L :

$$\frac{dE_L}{dC_L} = \frac{\alpha_E}{1 - e(1 - \lambda_C)} \left[\frac{E_L}{C_L} - \frac{1}{(C/E)_{CR}} \right]. \quad (5)$$

Eq. 5 can be solved in terms of the normalized variables $c = C_L(t)/C_L(0)$ and $\varepsilon = E_L(t)/E_L(0)$, with initial condition $\varepsilon(c = 1) = 1$ (e.g., Bender and Orszag 1987). This solution leads to the nutrient release curve:

$$\varepsilon(c) = c\beta_E \frac{(C/E)_{L,0}}{(C/E)_B} + \left[1 - \beta_E \frac{(C/E)_{L,0}}{(C/E)_B} \right] c^{\alpha_E/[1-e(1-\lambda_C)]} \quad (6)$$

where the subscript L,0 indicates carbon:nutrient ratios at the beginning of decomposition [i.e., $(C/E)_{L,0} = C_L(0)/E_L(0)$] and, for simplicity of notation, we defined

$$\beta_E = \frac{e(1 - \lambda_C)}{e(1 - \lambda_C) + \alpha_E - 1}. \quad (7)$$

When no leaching occurs and $\alpha_E = 1$, Eq. 6 can be simplified to

$$\varepsilon(c) = c \frac{(C/E)_{E,0}}{(C/E)_B} + \left[1 - \frac{(C/E)_{L,0}}{(C/E)_B} \right] c^{1/(1-e)}. \quad (8)$$

This is the same nutrient release curve derived by Manzoni et al. (2008a) for litter nitrogen. Eq. 8 had also been already derived in a different manner for a lumped model based on linear decomposition (Bosatta and Staaf 1982) and as a special solution of a continuum quality model including both nitrogen and phosphorus dynamics (Bosatta and Ågren 1991, Hyvonen et al. 2000). This outcome suggests that the compartmental structure of the decomposition model is of secondary importance with respect to macroscopic stoichiometric constraints when modeling decomposition of individual litter types. Notably, Eqs. 6 and 8 do not depend on the specific function used to model the decomposition flux (e.g., linear vs. nonlinear formulations for D ; see also Manzoni and Porporato 2007). This result similarly implies that the nutrient release curves are roughly independent of the climatic forcing and biochemical constraints on decomposition rates. The proposed model also assumes that the availability of inorganic nutrients only affects the rates of decomposition by modifying the flux D , while the stoichiometry of the decomposers, represented by Eq. 6, remains the same (Manzoni and Porporato 2007, 2009). In this manner, the roles of climate and external nutrient availability are separated from that of stoichiometry, thereby capturing the main mineralization patterns independent of specific climatic conditions at the decomposition site. However, climatic factors strongly affect the speed of the degradation process, resulting in faster convergence towards the condition $c = n = p = 0$.

Eq. 6 can be rearranged to present the litter carbon:nutrient ratio as a function of the fraction of remaining carbon (e.g., data presented in Fig. 4):

$$\frac{C_L}{E_L} = \left\{ \frac{\beta_E}{(C/E)_B} + \left[\frac{1}{(C/E)_0} - \frac{\beta_E}{(C/E)_B} \right] c^{\{\alpha_E/[1-e(1-\lambda_C)]\}-1} \right\}^{-1}. \quad (9)$$

From Eq. 9, the evolution of the litter N:P ratio as a function of remaining carbon can also be derived:

$$\begin{aligned} \frac{N_L}{P_L} = & \left\{ \beta_N (C/N)_B^{-1} + \left[(C/N)_{L,0}^{-1} - \beta_N (C/N)_B^{-1} \right] c^{\{\alpha_N/[1-e(1-\lambda_C)]\}-1} \right\} \\ & \div \left\{ \beta_P (C/P)_B^{-1} + \left[(C/P)_{L,0}^{-1} - \beta_P (C/P)_B^{-1} \right] \right. \\ & \left. \times c^{\{\alpha_P/[1-e(1-\lambda_C)]\}-1} \right\}. \quad (10) \end{aligned}$$

Projections of different trajectories of litter nitrogen and phosphorus evolution in the n - p space during decomposition are shown in Fig. 2 to illustrate the typical model behavior. All trajectories start at $c = n = p = 1$, and eventually reach the end of the decomposition process at $c = n = p = 0$. The shape of the particular trajectories depends on the initial conditions, with stronger immobilization ($n > 1$ or $p > 1$) occurring when residues are nutrient poor and initial net mineralization of nutrients (n and p) in richer litter monotonically decrease. The extent of the immobilization phase depends on the critical C/E ratio in Eq. 4, which increases with decreasing efficiency e (assuming that the decomposer elemental composition $(C/E)_B$, leaching rate λ_C , and preferential nutrient assimilation α_E are constant). Four possible regimes are observed. (A) The initial C:N and C:P ratios are both higher than the corresponding critical ratios (dotted-dashed gray curve in Fig. 2), and net immobilization of both nutrients occurs (n and $p > 1$) before net release is initiated (n and p decrease < 1). (B) The initial C:N ratio is higher than $(C/N)_{CR}$, while the initial C:P ratio is lower than $(C/P)_{CR}$ (solid gray line in Fig. 2); net nitrogen immobilization occurs at the beginning of decomposition, while phosphorus is released throughout the process. (C) The initial C:P ratio is higher than $(C/P)_{CR}$, while the initial C:N is lower than $(C/N)_{CR}$ (dashed gray line in Fig. 2), leading to net phosphorus immobilization and nitrogen release. (D) The initial C:N and C:P ratios are both lower than the corresponding critical ratios and net nitrogen and phosphorus mineralization occurs from the start of decomposition, with the trajectories remaining below one. This limiting regime may occur even in low-nutrient litters when decomposer carbon-use efficiency is also very low (black curves in Fig. 2). In fact, when e is low enough, the decomposer nutrient demand is decreased, and immobilization is less necessary. Under these conditions nutrients typically accumulate without net immobiliza-

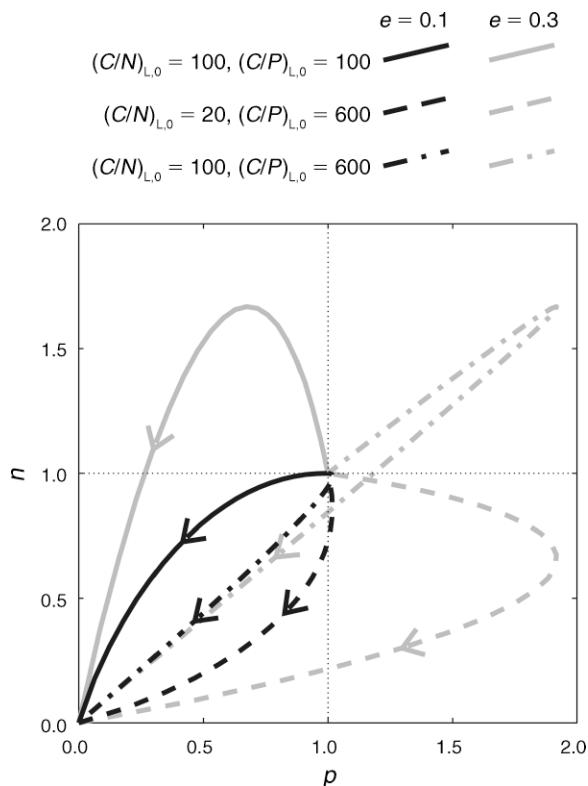


FIG. 2. Trajectories of litter decomposition in the n - p space (where n and p are the fractions of remaining N and P, respectively) for different litter types and decomposer carbon use efficiency e . (Solid black lines are characterized by lower efficiency than gray lines.) Each trajectory starts at $n = 1$, $p = 1$ and evolves in the direction indicated by the arrows. Solid lines illustrate the evolution of a phosphorus-rich, nitrogen-poor residue; dashed lines refer to a nitrogen-rich, phosphorus-poor residue; the dotted-dashed trajectory along the diagonal refers to a litter poor in both nitrogen and phosphorus. Decomposer composition is kept constant in each litter type [$(C/N)_B = 10$, $(C/P)_B = 50$], so that the critical C/E ratios are altered by varying only the carbon-use efficiency e .

tion (i.e., the concentration in the litter increases even with net nutrient release).

Estimation of model parameters

Eq. 6 has four parameters (e , $(C/E)_B$, α_E , and λ_C) that are assumed constant in time, although they may vary across litter types and climatic or site conditions. In this section we discuss which of the parameters may be assumed to be constant across data sets and which ones are more likely to change with litter type. The goal is to estimate at least some of the parameters a priori, and leave only a minimal number to be obtained through regression of the data.

There are no direct observations of carbon-use efficiency e for litter decomposers, and observations in aquatic bacteria and insects suggest a dependence on substrate nutrient concentration (Mattson 1980, Pandian and Marian 1986, del Giorgio and Cole 1998, Sterner and Elser 2002). Thus, given its possible variation across litter

types, we will consider e as a parameter to be fit to the data. The decomposer C:N ratio can be relatively well-constrained using data from the literature, with typical values ranging from ~ 7 in soils to ~ 15 in plant residues (Table 2). This range is considerably smaller than the range of substrate C:N, so that we can approximate it with a constant value $(C/N)_B = 10$ across litter types. To assess the sensitivity of this assumption, we also considered a power law dependence between decomposer and initial C:N ratio, based on the data reported in Table 2. Using the data for whole decomposer biomass and excluding the value $(C/N)_B = 24.8$ (considered unrealistically high, given the corresponding substrate C:N ratio), we found $(C/N)_B = 4.33 \times (C/N)_{L,0}^{0.22}$. In contrast, the microbial C:P ratio is more variable, with most values in the range of 10–60 in mineral soils, but with extreme values as low as five and as high as 500 (Fig. 3, Table 2). Moreover, precise information on litter decomposers is lacking, so that we cannot define a single $(C/P)_B$, or any function relating this parameter to litter chemistry and environmental conditions. Thus we will keep it as a parameter to be fit to the data.

The value of the leaching rate λ_C will likely vary with precipitation amount and intensity. In most ecosystems, leaching of organic carbon from the forest floor is $< 10\%$ of aboveground productivity, with little dependence on annual precipitation in the range of 500–2500 mm (Michalzik et al. 2001, Huxman et al. 2004). Respiration losses will thus be predominant in the long term, and we can set $\lambda_C \approx 0$ for that precipitation range without introducing substantial error. In contrast, sites with high precipitation rates (e.g., > 2500 mm) are prone to significant leaching losses (Cleveland et al. 2006, Goller et al. 2006, Schrumpp et al. 2006, Chang et al. 2007). This fact in turn increases their critical carbon:nutrient ratios (Eq. 4). Using data of litter mass loss and leaching under tropical humid conditions (Rees et al. 2006, Chang et al. 2007) we estimate that $\lambda_C \approx 0.5$ when annual rainfall is about 4000 mm/yr. These considerations suggest that leaching is (as expected) a highly nonlinear process, approximately negligible below a certain threshold of rainfall intensity but increasingly important above it. (A similar threshold-like nonlinearity is found in the commonly used term “field capacity,” which is used in hydrology as a good approximation to model percolation of water from the soil layer.) Thus, as a first approximation, we account for this increase by linearly interpolating λ_C between zero at 2500 mm/yr of rainfall to 0.5 at 4000 mm/yr. This approximation affected three data sets from humid tropical conditions (Chuyong et al. 2002, Hirobe et al. 2004, Xu 2006), resulting in values of λ_C between 0.06 and 0.45. Unlike λ_C , the parameter λ_E does not affect nutrient evolution curves because losses of organic nutrients are compensated by decomposer immobilization through the flux M_E (Eq. 1).

We estimated α_E by comparing observed and modeled dynamics toward the end of the decomposition process.

TABLE 2. Observed carbon : nutrient ratios (on a mass basis) of decomposer biomass growing in the field on different substrates.

Substrate type	Climatic regions	Decomposer		Substrate		Reference
		C:N	C:P	C:N	C:P	
Wood	TM		263†		~590	Cromack et al. (1975)
Wood	TM	14.6†	54†	~570	~5125	Edmonds and Lebo (1998)
Wood	TM	8.2		117.2		Hart (1999)
Wood	TM	22.4†				Hobbie et al. (2001)
Litter	TR	26.8†, 14.1‡	224†–102‡	18.2	285	Stark (1972)
Litter	TR	12.8†, 19†	197†, 199‡	19.7	837	Stark (1972)
Litter	TR	21.3†, 29.2‡	121†, 276‡	21.8	385	Stark (1972)
Litter	TM	6.3§, 10.7†, 23.9‡	81§, 100†, 242‡	54.6	100	Stark (1972)
Litter	BR	13.5	71.4	150		Baath and Soderstrom (1979)
Litter	BR	13.7		28.3		Wagener and Schimel (1998)
Litter	BR	9.8		~35		Schimel et al. (1999)
Litter	BR	11.6		41		Ross et al. (1999)
Litter	BR	13.5		48		Ross et al. (1999)
Litter	BR	13.6		40		Ross et al. (1999)
Litter	BR	24.8		75		Ross et al. (1999)
Litter	TM	9.2†				Hobbie et al. (2001)
Litter¶	TM	10.1	24.3	33.6	734.2	van Meeteren et al. (2008)
Litter	BR	5.5		27.2		Hannam et al. (2007)
Litter	BR	5.8		30.7		Hannam et al. (2007)
Litter + O layer	BR	7.1		27.6		Vance and Chapin (2001)
Litter + O layer	BR	8.3		28.2		Vance and Chapin (2001)
Litter + O layer	BR	6.4		25.5		Vance and Chapin (2001)
Litter + O layer	BR	12.4		51.4		Vance and Chapin (2001)
O layer	TM		73.5†, 297‡		~300	Cromack et al. (1975)
O layer	TM		116†, 333‡		~440	Cromack et al. (1975)
O layer	BR	10.7		22.1		Wagener and Schimel (1998)
Soil organic matter#	BR, TM, TR	7.37	23.0	12.3	72.0	Cleveland and Liptzin (2007)

Notes: Reported values are time and treatment averages for each substrate type, in each site. Climatic regions: BR, polar, subpolar, and boreal; TM, temperate; and TR, tropical and subtropical.

† Fungal sporocarps only; 50% carbon concentration is assumed.

‡ Fungal rhizomorphs only; 50% carbon concentration is assumed.

§ Slime mold only; 50% carbon concentration is assumed.

¶ Data from the first sampling date (two months after litterbag placement), characterized by an isolated peak in carbon : nutrient ratios, were excluded.

Carbon : nutrient ratios are averaged across all sites reported by Cleveland and Liptzin (2007).

In fact, α_E is analytically related to the asymptotic values (subscript L, ∞) of the carbon : nutrient ratios, $(C/E)_{L, \infty} = (C/E)_B \beta_E^{-1}$, which can be found from Eq. 9 in the limit of c tending to zero, by the following relationship:

$$\alpha_E = \lambda_C + (1 - \lambda_C) \left[1 + e \left(\frac{(C/E)_{L, \infty}}{(C/E)_B} - 1 \right) \right]. \quad (11)$$

All the fine-litter data seem to converge towards the same asymptotic C/E ratio values, with $(C/N)_{L, \infty} \approx 20$ and $(C/P)_{L, \infty} \approx 350$ (Fig. 4). Assuming, as a first order approximation, $\lambda_C \approx 0$, $(C/N)_B \approx 10$, $(C/P)_B \approx 50$, and $e \approx 0.25$ (Hyvonen et al. 2000), we find $\alpha_N \approx 1.25$ and $\alpha_P \approx 2.5$, indicating a marked preferential decomposition of phosphorus-rich compounds (when $\lambda_C > 0$, slightly smaller values for α_E are found). Similar values of α_E can also be found for wood, where higher asymptotic C/E ratios (Fig. 4) and lower decomposer carbon-use efficiency (as estimated by Manzoni et al. 2008a) balance each other. The value of α_N is close to one, suggesting that no preferential decomposition of nitrogen-rich substrates occurs. This result is also in agreement with the assumption $\alpha_N = 1$ used to model litter nitrogen dynamics by Manzoni et al. (2008a).

Data analysis

We first grouped the selected data sets according to the climatic region where they were decomposed (Table 1) and then converted them to the normalized variables $c = C_L(t)/C_L(0)$, $n = N_L(t)/N_L(0)$, and $p = P_L(t)/P_L(0)$. A preliminary inspection of the data revealed that, in general, relevant mass or nutrient losses in the early decomposition phase did not occur, but the initial condition evolved approximately continuously along the decay trajectory. Some data sets showed an initial sharp decrease of nutrient content (phosphorus in particular) with respect to the initial concentration. Where it did occur, we accounted for this loss by modifying the initial condition of the litter, as suggested by Aber and Melillo (1980) and Berg and Staaf (1987). When the first observed n and p values were lower than the threshold 0.9 and lay below the 1:1 line in the n - c or p - c plots (meaning that nutrient losses occurred faster than carbon losses), we set C/E at that first point as a new initial condition, approximating a rapid leaching event that decreases the initial nutrient content. Six decomposition series from tropical sites showed a leaching phase that lasted until about 50% of the mass was lost, and these were not considered in this analysis. We also

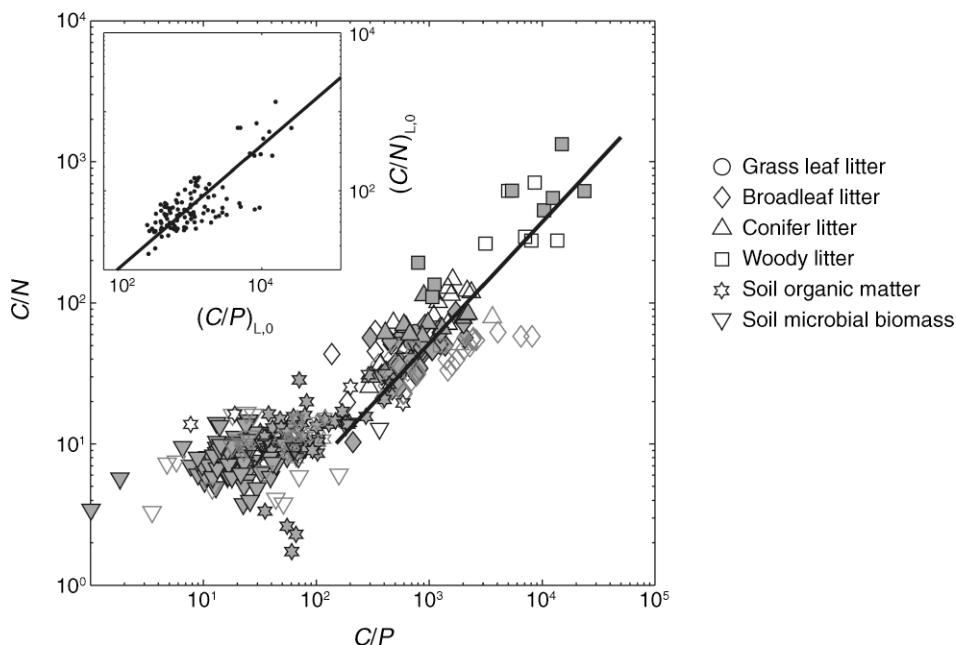


FIG. 3. Initial elemental composition (on a mass basis) of the plant residues used in this study, compared to the composition of soil organic matter and soil microbial biomass (soil data after Cleveland and Liptzin [2007]). Litter types are indicated by different symbols; climatic conditions by different codes (open black symbols represent polar, subpolar, and boreal regions; solid gray, temperate regions; open gray, tropical and sub-tropical regions). Inset: initial composition for all litter types and origins (denoted by subscript $L,0$, and already accounting for initial leaching), and Type II least-squares regression of the log-transformed data.

excluded a decomposition series where immobilization of nitrogen occurred regardless of the very high initial nitrogen concentration (alder leaves in Berg and McLaugherty 1989).

After accounting for the initial loss, the selected data sets were used to obtain the free parameters e and $(C/P)_B$ in Eq. 6 through numerical nonlinear regressions. The nonlinear regression was performed in two steps. Following Manzoni et al. (2008a), we obtained the carbon-use efficiency using the $n(c)$ curve, where all the other parameters are fixed. As a second step, we used the obtained e and found $(C/P)_B$ from the $p(c)$ curve. Finally, the generalized critical carbon:nutrient ratios for the different litter types and climatic conditions were computed from Eq. 4.

RESULTS

General patterns of nutrient immobilization and release

The initial elemental mass ratios of the litter used in our analysis reveal both a broad range and fundamental constraints in their stoichiometry (Figs. 3 and 4). Clearly, woody residues (open squares) have the lowest nutrient concentrations in the data set, followed by conifer foliage (open triangles). Litter from grasses (open circles) and deciduous tree (open diamonds) have generally higher nutrient concentrations, with the exception of foliage collected in tropical regions that are often poor in phosphorus. Despite relatively low phosphorus concentration in some tropical litters, the log-transformed initial C:N and C:P ratios are strongly

correlated (Fig. 3, inset; $(C/P)_{L,0} = 10.15 \times (C/N)_{L,0}^{1.16}$, $R = 0.77$, $P < 0.0001$), indicating that in general litters are similarly rich (or poor) in both nutrients. For comparison, the same elemental mass ratios for soil organic matter (star symbol) and soil microbial biomass (inverted triangle symbol; soil data from Cleveland and Liptzin 2007) are also shown in Fig. 3, illustrating the progressive increase of nutrient concentrations along the continuum from plant residues to soil organic matter and decomposer biomass.

The ratios of carbon:nutrients and N:P of all litter types change through time as a function of the fraction of decomposed carbon (Fig. 4). The large difference in nutrient concentrations between the decomposers and their substrates at the beginning of decomposition drives the immobilization of nitrogen and phosphorus in litter (Berg and McLaugherty 2003). As decomposition proceeds, this difference decreases, as shown clearly by the decreasing trend of litter carbon:nutrient ratios toward the values $(C/N)_{L,\infty} \approx 20$ and $(C/P)_{L,\infty} \approx 350$. Nutrient dynamics in woody residues tend to be more variable than in fine litters, partly due to order-of-magnitude differences in initial conditions and widely different leaching patterns. Also, intrinsic uncertainties in the chronosequence method introduce higher variability in the observations with respect to the litterbag studies. In general, the immobilization phase is longer in woody residues, and the carbon:nutrient ratios seem to converge slowly to the values typical of fine litter (Fig. 4). The N:P ratio of both fine litter and woody residues

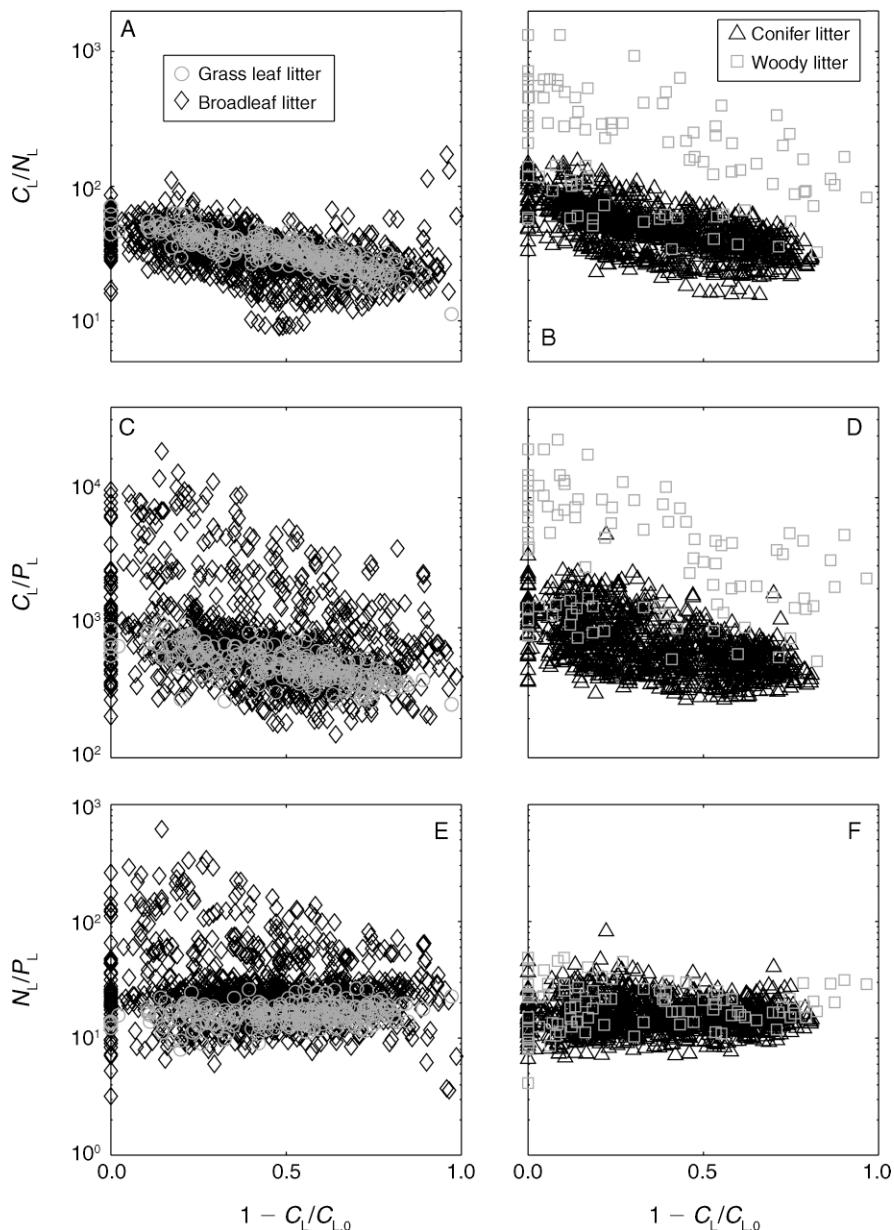


FIG. 4. C:N (top panels), C:P (middle panels), and N:P (bottom panels) ratios for all data (grass and broadleaf tree litter in the left panels [A, C, E]; conifer and woody litter in the right panels [B, D, F]) as a function of the fraction of decomposed carbon, $1 - C_L(t)/C_{L,0}$. The data sets are described in more detail in Table 1; all ratios are expressed on a mass basis.

converges to a value of ~ 20 , as observed previously in long-term decomposition studies (Laiho and Prescott 2004, Moore et al. 2008).

As described by our model (Fig. 2), the patterns of nitrogen and phosphorus immobilization and mineralization of individual litter species change dramatically as a function of litter initial conditions and decomposer characteristics. Four regimes in the $n-p$ plane can be characterized, each with a different combination of initial carbon:nutrient ratios. Fig. 5 shows an example of model fitting to the decomposition data for each

regime (see *Methods: Data analysis* for details), illustrating how changes in carbon-use efficiency and decomposer C:P ratio control the shape of the nutrient release curves. In the tropical data set of Thompson and Vitousek (1997), nitrogen is immobilized from the beginning of decomposition (when n and p are still close to one), while phosphorus is released (Fig. 5A). In this case, $(C/N)_{CR}/(C/N)_{L,0} < 1$ and $(C/P)_{CR}/(C/P)_{L,0} > 1$. Fig. 5B, carbon shows two more tropical decomposition data sets, from Chuyong et al. (2002) and Isaac and Nair (2005); the former shows net release of both nutrients

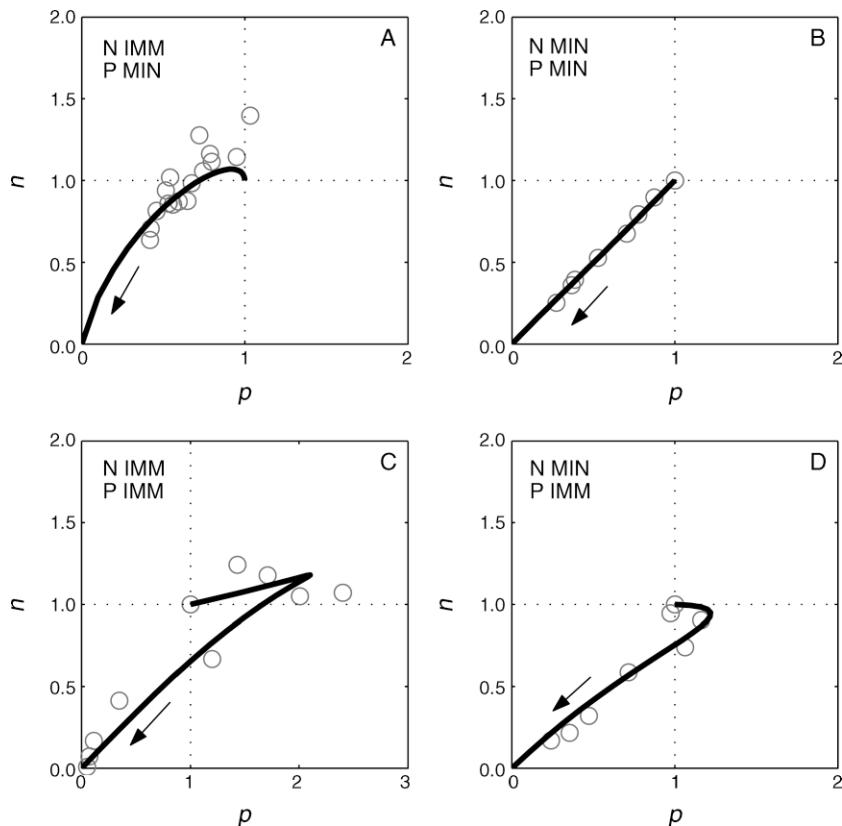


FIG. 5. Sample trajectories of litter decomposition in the n - p space, for different critical carbon : nutrient ratios and litter types (time evolves in the direction of the arrows). The four possible combinations of $(C/E)_{CR}$ and $(C/E)_{L,0}$ result in different initial nutrient immobilization or mineralization (see also Fig. 7). Data sources: (A) Thompson and Vitousek (1997); (B) Chuyong et al. (2002); (C) Isaac and Nair (2005); and (D) Li et al. (2007). Solid thick lines are model results (Eq. 6).

(Fig. 5B) while the latter shows immobilization of both initially (Fig. 5C), indicating that the critical carbon : nutrient ratios were lower than the corresponding initial C/E ratios. Fig. 5D illustrates the case of phosphorus immobilization and nitrogen release, which occurs in some litters that are relatively poor in phosphorus and rich in nitrogen (Li et al. 2007).

Decomposer stoichiometric parameters

Based on a theoretical framework, our analytical model captures the different stoichiometric trajectories of decomposition shown in Fig. 5 quite well. A similar close fit is achieved with the global data set where the only free parameter e , the carbon-use efficiency, explains most of the variance in the nitrogen evolution curves ($R^2 = 0.96$, $P < 0.0001$; Fig. 6A) while the combination of e and $(C/P)_B$ is sufficient to describe the corresponding phosphorus dynamics ($R^2 = 0.90$, $P < 0.0001$; Fig. 6B).

Variability in the carbon-use efficiency e is largely explained by the initial litter C:N ratio (Fig. 7A; $e = 6.25 \times (C/N)_{L,0}^{-0.77}$, $R^2 = 0.65$, $P < 0.0001$), resulting in a strong power law dependence of the critical C:N ratio on the initial C:N ratio (Fig. 7C; $(C/N)_{CR} = 2.33 \times (C/N)_{L,0}^{0.75}$, $R^2 = 0.64$, $P < 0.0001$). We also assessed

the effects of another index of litter quality, the acid unhydrolyzable fraction (so called “lignin”), on the estimated carbon-use efficiencies. The parameter e is not correlated with the initial concentration of acid unhydrolyzable fraction ($R = -0.06$, $P > 0.1$), allowing us to focus on the stoichiometric controls, and neglect the role of chemical recalcitrance.

Most of the variability in the phosphorus evolution during decomposition is also captured by changes in e , with a residual effect of $(C/P)_B$ (Fig. 7B; $(C/P)_B = 14.3 \times (C/P)_{L,0}^{0.26}$, $R^2 = 0.24$, $P < 0.0001$). As in Fig. 7C, the combined effects of e and $(C/P)_B$ leads to a strong power law dependence of the critical C:P ratio on the initial C:P ratio (Fig. 7D; $(C/P)_{CR} = 2.27 \times (C/P)_{L,0}^{0.84}$, $R^2 = 0.83$, $P < 0.0001$). When the parameter $(C/N)_B$ is allowed to vary with initial litter C:N ratio, we still find a significant negative correlation between carbon use efficiency and initial litter C:N ratio (Fig. 7A, dashed line; $e = 2.58 \times (C/N)_{L,0}^{-0.55}$, $R^2 = 0.49$, $P < 0.0001$), although the slope of the relationship is smaller. These differences are mirrored by the relationship between the estimated $(C/P)_B$ and $(C/P)_{L,0}$, which becomes steeper (Fig. 7B, dashed line; $(C/P)_B = 5.40 \times (C/P)_{L,0}^{0.40}$, $R^2 = 0.52$, $P < 0.0001$).

As a result of the relationships between critical and initial ratios, the patterns of initial nutrient mineralization or immobilization depend not only on litter type and composition, but are also mediated by decomposer characteristics. To illustrate these effects we normalize the critical C/E ratios with respect to the litter initial C/E ratios, and plot them in a $(C/N)_{CR}/(C/N)_{L,0} - (C/P)_{CR}/(C/P)_{L,0}$ plane (Fig. 8). Although the variability of the data points is large, $(C/N)_{CR}/(C/N)_{L,0}$ and $(C/P)_{CR}/(C/P)_{L,0}$ are significantly and positively correlated ($R = 0.63$, $P < 0.0001$). Values >1.0 on either axis indicate that $(C/E)_{CR}$ is higher than $(C/E)_{L,0}$, corresponding to a net release of the nutrient E from the beginning of decomposition. The correlation of initial litter C:N and C:P ratios (Fig. 3), with high nutrient litters characterized by low C:N and C:P ratios, and nutrient-poor litters characterized by higher ratios, allows us to further generalize and explore the patterns of mineralization and immobilization based on the initial nutrient concentrations. To do this, the regressions in Fig. 7C, D for the critical C/E ratios are combined with that of Fig. 3 relating the initial conditions. The result is a parametric relationship in the $(C/N)_{CR}/(C/N)_{L,0} - (C/P)_{CR}/(C/P)_{L,0}$ plane (solid black line in Fig. 8):

$$\frac{(C/P)_{CR}}{(C/P)_{L,0}} = 0.87 \left[\frac{(C/N)_{CR}}{(C/N)_{L,0}} \right]^{0.77} \quad (12)$$

which describes the tendency of plant residues where the initial C:N and C:P ratios are related (Fig. 3, inset) to mineralize either nitrogen or phosphorus at the beginning of decomposition.

DISCUSSION

Variability of the decomposer carbon-use efficiency

As demonstrated by Figs. 2 and 5, the most important factors controlling the shape of the nutrient release curves are the initial and critical carbon : nutrient ratios. The critical ratio has been interpreted mathematically as a function of decomposer biochemical characteristics (Bosatta and Staaf 1982, Ågren and Bosatta 1996, Manzoni and Porporato 2007). Here we extended the previous models of $(C/E)_{CR}$, including the role of physical losses of organic matter from the litter and the possible preferential decomposition of nutrient-rich compounds. These physical and chemical factors are accounted for in the parameters λ_C and α_E , respectively (Eq. 4). The last two parameters can be assumed to be negligible or relatively constant (with the exception of high λ_C in humid conditions; see *Methods: Estimation of model parameters*) so that the variability in the critical ratios across litter types can be mostly attributed to the efficiency e and the decomposer elemental composition (Fig. 7A, B).

Some modeling analyses have assumed that the carbon-use efficiency is constant, while $(C/N)_B$ varies across litter types (Hyvonen et al. 2000, Nicolardot et al.

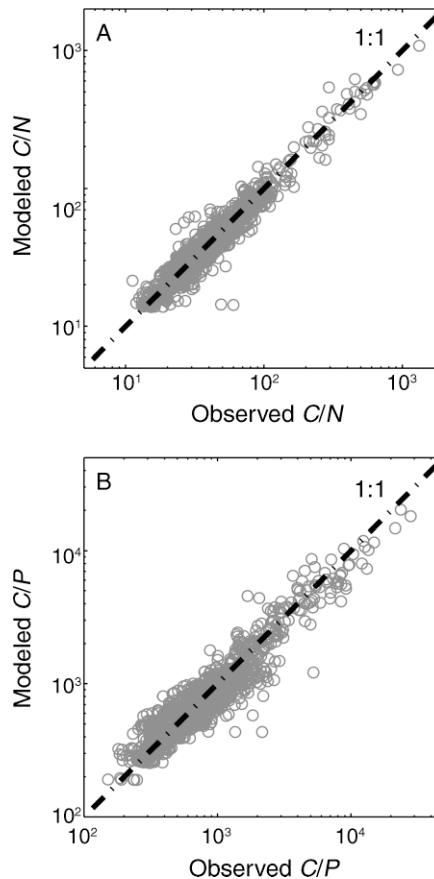


FIG. 6. Scatter plot of modeled vs. observed (A) carbon : nitrogen and (B) carbon : phosphorus ratios.

2001). The $(C/N)_B$ values necessary to describe the observed nutrient mineralization patterns assuming constant carbon-use efficiency would range between about two to nearly 100 (in nutrient-rich and nutrient-poor residues, respectively). Such a range seems unrealistically wide, since observed changes in microbial C:N ratio are well-constrained across a variety of soil organic matter substrates (Fig. 1; Cleveland and Liptzin 2007), and small long-term responses have been observed after amending soils with different organic materials (Bremer and Vankessel 1992, Mueller et al. 1998). Data on litter microbial C:N ratios in natural conditions are sparser than in mineral soils, although they consistently fall in the range of 8–15 (Table 2), even in low nitrogen partly decomposed wood ($(C/N)_B = 8.2$; Hart 1999). The whole decomposer community, encompassing both microbial and faunal groups with $(C/N)_B \approx 4-10$ (Hunt et al. 1987), is expected to have an overall C:N ratio smaller than a fungal-dominated community ($(C/N)_B \approx 15$), and the assumption of a constant value $(C/N)_B = 10$ seems to be reasonable for the present large-scale analysis. The results obtained when relaxing this assumption and allowing $(C/N)_B$ to increase with

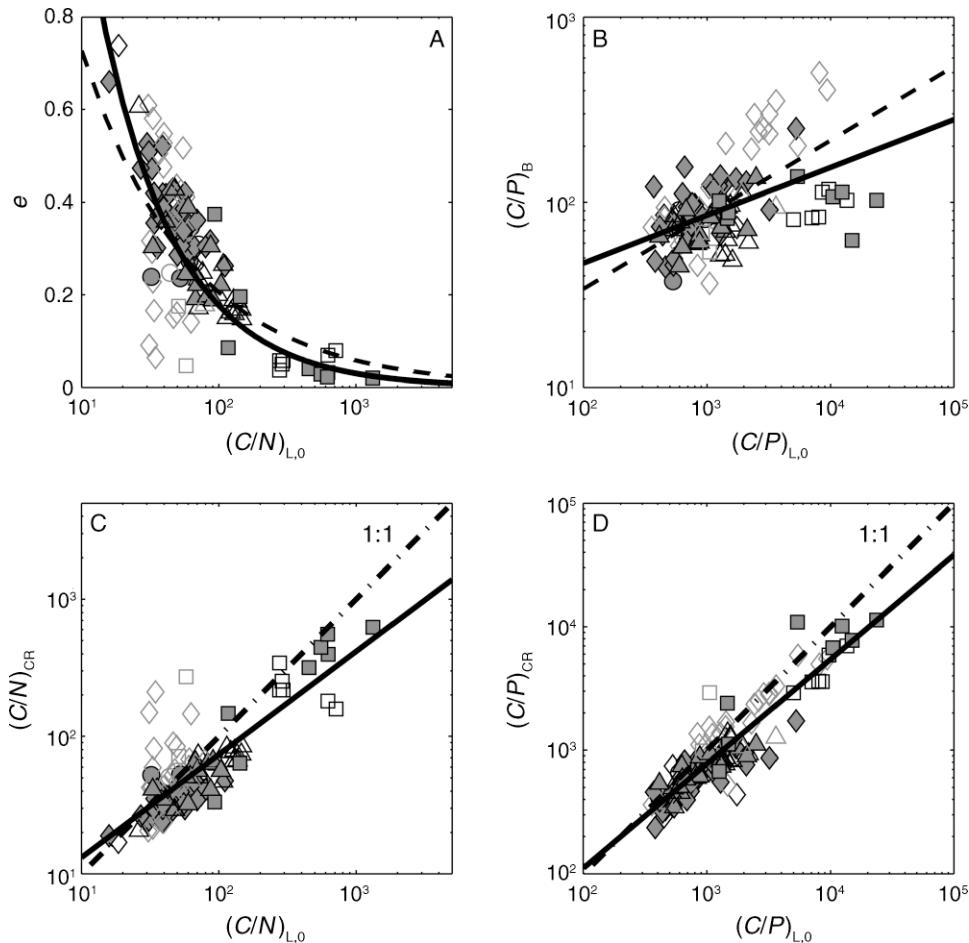


FIG. 7. (A) Decomposer carbon-use efficiency e and (C) critical C:N ratio as a function of initial litter C:N, as well as (B) decomposer C:P ratio and (D) critical C:P ratios as a function of initial litter C:P for different litter types and climatic regions (symbols and codes as in Fig. 3). Initial litter C/E already accounts for the initial leaching phase. Solid lines are linear least-squares regressions of the log-transformed data when $(C/N)_B = 10$; dashed lines refer to the case $(C/N)_B = 4.33 \times (C/N)_{L,0}^{0.22}$ (corresponding data points are not shown).

$(C/N)_{L,0}$ (based on the limited data reported in Table 2) are similar.

Accordingly, we attribute most of the variability in $(C/N)_{CR}$ to changes in the decomposer carbon-use efficiency e (Fig. 7A), on the basis that more efficient carbon use occurs when nutrients in organic forms are more available, while $(C/N)_B$ is relatively constant (Manzoni et al. 2008a). This is in agreement with modeling studies showing a positive correlation between litter decomposer efficiency and nitrogen content of humus underlying the litter layer (d'Annunzio et al. 2008), and with decreases in efficiency observed in consumers in terrestrial and aquatic environments when substrate nutrient concentration is low (Mattson 1980, Pandian and Marian 1986, del Giorgio and Cole 1998, Elser et al. 2000). From a physiological perspective, decreased efficiency might be related to regulation of catabolic reactions (Russell and Cook 1995), or increased energy use for nutrient mining through

increased exoenzyme production (Craine et al. 2007, Sinsabaugh et al. 2008). Additional energetic costs may also result from asymbiotic nitrogen fixation (Vitousek and Howarth 1991, Vitousek and Hobbie 2000), which contributes up to 10% of the total nitrogen immobilized in decomposing residues (Thompson and Vitousek 1997). Nitrogen fixation tends to be higher in easily decomposable litter with low N:P ratio, where the nitrogen demand is higher (Vitousek and Hobbie 2000, Reed et al. 2007), consistent with the increasing respiration costs shown in Fig. 7A.

The fact that the decomposer carbon-use efficiency increases with the initial organic nitrogen concentration of the litter is also connected to the effects of inorganic nutrient availability on decomposer metabolism. When litters have low initial C:N ratios, net mineralization prevails and the inorganic nitrogen pool increases; in contrast, available inorganic nitrogen in nitrogen-poor litters is likely very low because of strong immobiliza-

tion. Hence, there is a positive correlation between organic nitrogen in decomposing litter and inorganic nitrogen availability in the litterbags and their surroundings. In principle, both organic nitrogen and inorganic nitrogen could affect the carbon-use efficiency in a similar way (i.e., by decreasing the efficiency when nutrient availability is low). The small or negative effects of nitrogen fertilization on respiration rates that have been observed (e.g., Fog 1988, Hobbie and Vitousek 2000, Craine et al. 2007) could be explained by decreased carbon-use efficiency when inorganic nitrogen is limiting, as also suggested by a theoretical study (Ågren et al. 2001). Moreover, limited inorganic nitrogen due to CO₂ enrichments has been shown to enhance carbon losses due to altered microbial activity (Gill et al. 2006). These pieces of evidence indirectly support our hypothesis of reduced efficiency with increased initial litter C:N ratio.

The quality of litter carbon could also affect the decomposer carbon-use efficiency. The investment in enzyme production increases with the complexity of the substrates, ranging from simple soluble compounds to the more recalcitrant compounds such as cellulose, hemicellulose, tannins, waxes, and lignin (Berg and McClaugherty 2003). Consistently with the larger carbon costs to degrade complex substrates, theoretical studies generally assume that e decreases with the degree of recalcitrance (Ågren and Bosatta 1996, Moorhead and Sinsabaugh 2006). Hence, during decomposition, changes in litter chemical composition may become an important driver for e . However, we did not find any significant relationship between the estimated long-term e and the initial concentration of acid unhydrolyzable fraction in litters from our database, suggesting that the stoichiometric constraints may be stronger than the litter chemical features in the long term and at the larger scale we investigated.

Variability of the decomposer C:P ratio

After obtaining the carbon-use efficiency from the nitrogen release curves, we used the phosphorus release curves to estimate the parameter $(C/P)_B$ (Fig. 7B). The effects of organic phosphorus availability on decomposer composition and activity have been rarely studied. We found values in the 20–100 range for most ecosystems, with increasingly higher values in phosphorus-poor residues (in particular in some tropical litters and wood residues, Fig. 7B). A similar pattern arises regardless of the assumed dependency of $(C/N)_B$ and $(C/N)_{L,0}$, although $(C/P)_B$ increases faster with $(C/P)_{L,0}$ when part of the variability in the critical C:N ratio is attributed to changes in $(C/N)_B$ (dashed line in Fig. 7B). Although the estimated values are, on average, higher than the ones observed in mineral soils (Fig. 3, Table 2), they are generally not unrealistic, given the high variability of this parameter in natural conditions, and the high C:P ratios observed in litter and wood decomposing fungi, in particular in the tropics (Stark

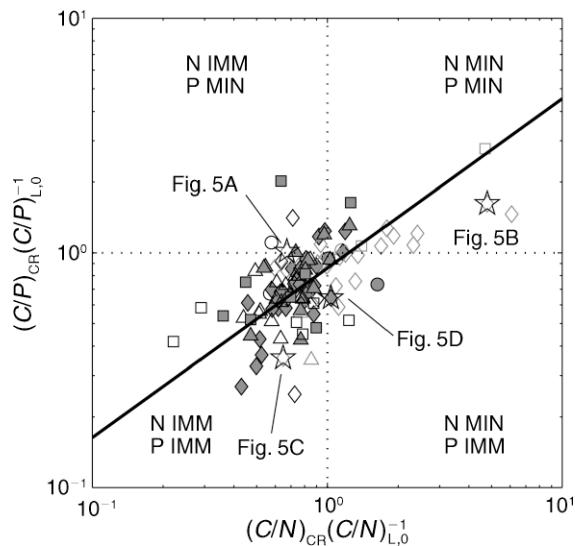


FIG. 8. Patterns of initial nutrient mineralization (MIN) or immobilization (IMM) as a function of litter type and climatic region (symbols and codes as in Fig. 3). Each point in the plot represents a litter data set in terms of its critical and initial carbon:nutrient ratios. When the critical carbon:nutrient ratio is larger than the initial carbon:nutrient ratio [i.e., $(C/N)_{CR}/(C/N)_{L,0} > 1$ or $(C/P)_{CR}/(C/P)_{L,0} > 1$], net mineralization occurs; otherwise net immobilization is needed. The points corresponding to the four combinations of initial mineralization and immobilization shown in Fig. 5 are indicated by stars. The solid black line represents the mineralization conditions for litters where the initial C:N and C:P ratios are perfectly correlated (Fig. 3), and the critical ratios are given by the regressions in Fig. 7 (Eq. 12).

1972, Cromack et al. 1975). Only few litter types from a tropical humid site (Hirobe et al. 2004) and wood decomposition data sets resulted in unrealistically high $(C/P)_B$ (Fig. 7B). Such values are likely not indicative of real decomposer composition but rather a result of the fact that in these ecosystems phosphorus release is extremely fast, even if the initial concentration is low, thus giving rise to very high values of the critical C:P ratio (Fig. 7D). In fact, our method attributes all the variability in the phosphorus release curves to e and $(C/P)_B$, while it is also possible that some of the variability could be explained by higher values of α_P or λ_C in particular sites or litter types.

Moreover, site effects other than precipitation (e.g., soil nutrient availability and microclimatic conditions) may affect the patterns of nutrient release and accumulation and hence the critical ratios. As shown by reciprocal litterbag experiments, sites with higher nutrient availability tend to have larger nutrient accumulation in a given litter type (Thompson and Vitousek 1997, Hobbie and Vitousek 2000, Moore et al. 2006), resulting in lower critical carbon:nutrient ratio. In turn this would suggest higher carbon-use efficiency in nutrient-rich sites, consistent with theoretical studies (Ågren et al. 2001).

*Stoichiometric and climatic controls
of the critical C/E ratios*

As already noted in the case of nitrogen (Manzoni et al. 2008a), the estimated critical ratios (Eq. 4) of both nitrogen and phosphorus correlate well with the initial carbon:nutrient ratios in each litter type and in every climatic region (Fig. 7C, D). The values of $(C/E)_{CR}$ that had been estimated in previous works from decomposition data are in agreement with our results for both tropical (Seneviratne 2000) and mid to high latitude data sets (Berg and McClaugherty 1989, Moore et al. 2006). No significant correlation between the critical C/E ratios and climatic region appears in mid to high latitudes, so that most of the variability can be attributed to the initial ratios $(C/N)_{L,0}$ and $(C/P)_{L,0}$ in those regions. Tropical sites with high rainfall have critical ratios that are generally higher for a given initial condition (Fig. 7C, D). Our results suggest that the compound effects of increased decomposer respiration, high decomposer C:P ratio, and physical losses (in particular leaching of organic matter under high rainfall regimes) may lead to these high critical ratios, which imply a tendency to release of nitrogen and phosphorus even from very nutrient-poor residues.

The fact that $(C/E)_{CR}$ are not constant but increase with initial C/E ratio implies that residues with low initial nutrient concentration may have a relatively short immobilization phase. For instance, woody residues initially immobilize both nitrogen and phosphorus (lower left quadrant in Fig. 8), although quite surprisingly they also start releasing these nutrients at high C/E ratios (Hart 1999, Krankina et al. 1999). According to our results, this is possible because of the consistently low carbon-use efficiency of wood decomposers. Most conifer litters also tend to immobilize both nutrients in the first stages of decomposition, although a few showed initial net release. Deciduous tree and grass foliage showed different behaviors depending on their chemical characteristics and climatic conditions. Only a few deciduous species and grasses are able to release both nitrogen and phosphorus throughout decomposition because of their low initial C:N and C:P ratios or particularly high critical ratios (upper right quadrant in Fig. 8). In boreal and temperate climates, nitrogen tends to be immobilized (left quadrants), while it is generally released in tropical areas (right quadrants). Similarly, phosphorus is typically immobilized in boreal and temperate regions, while it may be immobilized or released in the tropical ones, depending on the initial condition.

Most residues are either relatively poor in nitrogen and phosphorus, or they are relatively rich in both nutrients. Nutrient-poor litters (regime A; lower left quadrant in Fig. 8) immobilize both nitrogen and phosphorus, while nutrient-rich litters (regime D; upper right quadrant in Fig. 8) release the two nutrients. This pattern mirrors the strong correlation between initial C:N and C:P ratios (Fig. 3), and results in rare co-

occurrence of phosphorus mineralization and nitrogen immobilization, or nitrogen mineralization and phosphorus immobilization (Eq. 12). Remarkably, the few tropical plant residues with particularly high initial N:P ratio, which might be expected to release nitrogen and immobilize phosphorus, tend to behave similarly to litters richer in phosphorus. As a consequence, the N:P ratio alone in these cases does not predict which of the two nutrients is released first. This result can be explained by the combination of low carbon-use efficiency, unusually high $(C/P)_B$, and possibly significant leaching losses, which lead to high enough values of $(C/P)_{CR}$ to allow phosphorus release even from residues with a very high N:P ratio.

Evaluation of model assumptions

The mass balance equations that describe carbon and nutrient dynamics in the litter (Eqs. 2, 3) account for biological processes in a simplified but realistic way. The assimilation of nitrogen and phosphorus from both organic (plant residues) and inorganic sources is described in the model through the net mineralization fluxes (Eq. 1). The net fluxes are sufficient to compute the mass balances of the litter nutrient pools, but neglect the physiological differences in the assimilation pathways of these two nutrients. Nitrogen is directly assimilated from the organic sources in the form of amino acids, from which ammonium is released through endogenous deamination (Swift et al. 1979, McGill and Christie 1983), while organic phosphorus is first mineralized to orthophosphate ions by extracellular enzymes and then immobilized (Sinsabaugh et al. 1993, Plante 2005). These physiological differences may lead to different patterns of gross nutrient mineralization and immobilization, with larger gross fluxes associated with phosphorus assimilation. In turn, large gross immobilization is often related to strong nutrient limitation, which may inhibit the decomposition process (Manzoni and Porporato 2007, 2009). However, the goal of the model is to describe the stoichiometric evolution of decomposing litter regardless of the speed of the process, so that modeling the net fluxes exchanged between the decomposer biomass and the inorganic pools is sufficient. This allows us to avoid a detailed description of gross mineralization and immobilization fluxes (Parton et al. 1988, Bosatta and Ågren 1991, Manzoni et al. 2008a).

The mathematical description of leaching losses of organic carbon and nutrients is also simplified. We assumed that leaching can be described by a rapid initial loss of organic nitrogen and phosphorus, which is followed by prolonged low-intensity losses. Since fresh plant residues have a pool of readily soluble materials, leaching will likely be larger early during decomposition, while long-term physical losses may be less significant (Berg and McClaugherty 2003, Cleveland et al. 2006). We estimated that in 43% of the data sets the initial phosphorus loss was larger than the nitrogen loss, while the reverse was true in 7% of the analyzed cases. This

result is not surprising, as the initial loss of organic nitrogen is generally lower than the loss of phosphorus, which is particularly important in humid Nordic ecosystems (Berg and Staaf 1987, Blair 1988, Berg and Cortina 1995, Berg and McLaugherty 2003) and tropical ecosystems (Hirobe et al. 2004, Isaac and Nair 2005). We also assume that leaching may persist during decomposition, and we model these nutrient losses as proportional to the decomposition flux by means of a constant λ_C (e.g., Currie and Aber 1997). The rationale behind this choice is that organic substrates are made available by the activity of the decomposers at a rate D (Fig. 1).

Our assumptions that the decomposer biochemical characteristics, e and $(C/E)_B$, are constant in time may be justified by the focus on long-term patterns of mineralization (i.e., monthly and yearly time scales in tropical and temperate climates, respectively) across widely different litter types. The parameters e and $(C/E)_B$ may be interpreted as time-averaged characteristics representative of the whole decomposer community and of its response to litter type. This assumption is also in agreement with long-term experimental observations (Hart et al. 1994, van Meeteren et al. 2008), and previous modeling studies (Hyvonen et al. 2000). Moreover, although some temporal trends of microbial elemental composition may occur (e.g., Wagener and Schimel [1998] found decreasing microbial C:N ratio from the fresh litter to the O horizons in a forest floor chronosequence), the range of C:N ratio variability found is relatively small and does not, in our opinion, justify a more complicated model structure at the level of resolution of this study.

The proposed model also neglects the transport of organic compounds by mycorrhizal fungi and roots. This pathway of nutrient export from the litter has been shown to be important in the temporal dynamics of nitrogen and phosphorus supplies to plants (Trofymow and van den Drieesche 1991); however, it does not seem to be significant from the perspective of litter mass balances and stoichiometry. In fact, the presence of fine roots and mycorrhizae in the litterbag tends only to accelerate decomposition in some ecosystems, but it does not appear to affect the evolution of carbon:nutrient ratios during the process (Cuevas and Medina 1988, Zhu and Ehrenfeld 1996, Chuyong et al. 2002, Luizao et al. 2007).

Modeling nutrient mineralization in soils and aquatic systems

We developed our model to describe nutrient mineralization patterns in aboveground plant residues decomposing in terrestrial ecosystems. Nevertheless, similar biological and physical processes also control nutrient accumulation and release from organic matter decomposing in mineral soils as well as plant residues decomposing in aquatic systems. A formally similar solution to Eq. 8 was derived by Ågren and Bosatta (1996) to describe the evolution of homogeneous plant

residues into soil organic matter compounds. Similarly, Eq. 8 can be directly applied to describe organic matter dynamics in soils where the interactions of fresh residues and more stabilized compounds can be neglected. When soil spatial and chemical heterogeneities are important and nutrients are actively recycled between nutrient-rich and poor patches (e.g., in litter-amended soils), mineralization can still be described rigorously by lumped models as in Eqs. 6 or 8, provided that a suitable parameterization of decomposer stoichiometry is used (Manzoni et al. 2008b). The presence of dissolved organic matter leaching from the litter layer and its interaction with humic compounds and soil decomposers (Michalzik et al. 2001) could also be added in the mass balances in Eqs. 2 and 3.

The improved model could also be used to describe plant residue decomposition in wetlands, streams, or estuarine and marine systems. In such systems the patterns of immobilization and mineralization as a function of carbon loss qualitatively follow the same patterns observed in terrestrial systems (Gulis and Suberkropp 2003, Moore et al. 2005, 2008, Davis et al. 2006). Similarly to mineral soils, however, in aquatic systems the flux of dissolved organic matter entering the litter pool through water flow will sometimes be important. Accordingly, the present model could be applied in aquatic systems only where such external inputs of organic compounds are not significant.

CONCLUSIONS

Using a simplified mathematical model we have shown that decomposers are indeed “integrators of the various element cycles” (Plante 2005). The dynamics of carbon, nitrogen, and phosphorus in plant litter worldwide, mediated by decomposer activity, result in clear patterns of nutrient immobilization and release that depend on the chemical characteristics of the litter and the stoichiometric requirements of the decomposers. Our results suggest that the critical C:N and C:P ratios, below which nutrients are released, increase with decreasing initial litter nitrogen and phosphorus concentrations. From the theoretical definition of critical carbon:nutrient ratios, we suggest that this pattern can be explained by reduced decomposer carbon-use efficiency and, in tropical regions, by increased decomposer C:P ratios and higher leaching rates. These factors allow nutrient release from plant residues with low nutrient concentrations, in particular in tropical regions. As a consequence, in tropical systems the litter N:P ratio alone may not be a reliable index to predict which nutrient is released first during decomposition. Specific observations of microbial carbon:nutrient ratios in litters from different climatic regions will help to test these results.

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