



Supporting Online Material for

The Global Stoichiometry of Litter Nitrogen Mineralization

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Supporting Online Materials and Methods

1 Carbon-nitrogen relationships in decomposing litter

The relationship between the carbon and nitrogen contents in decomposing plant residues has been extensively studied for its importance in controlling nutrient availability in natural and managed ecosystems (1-4). Early studies recognized a linear relationship between N concentration and mass (or carbon) loss (5-7), suggesting that N accumulates while C is lost from the litter. N accumulation depends on three main factors: i) microbial immobilization during growth, ii) bonding of N to aromatic compounds, and iii) chemical fixation of external N (e.g., soil inorganic N or added N from fertilization) to low-N fresh litter (8). N immobilization by decomposers is generally considered the predominant accumulation factor during the initial and more active phase of decomposition, until mass loss reaches about 70% (1). Chemical fixation of inorganic N may be important in sites with large sources of exogenous inorganic N (e.g., fertilization, fallow fields), while here we will focus on natural ecosystems where the primary external sources of N are from canopy throughfall and atmospheric deposition. In general, N losses from the plant residues are controlled by both biological and physical factors. However, leaching of organic compounds is typically less important than biological decomposition (9) and the predominant pathway of N loss is through decomposer mineralization by the decomposers and subsequent leaching of N in inorganic forms.

Since here we focus on natural systems where physical processes do not significantly affect the stoichiometry of residue decomposition, we can consider the predominant biological factors only. Waksman (10) was among the first to recognize that the nutrient requirements of the decomposer community had to be met before the organic matter in the soil releases the nutrients necessary for plant growth. Also the linear relationship between carbon and nitrogen contents in decomposing litter can be explained by considering the stoichiometric requirements of the decomposers (7), as clearly formalized by earlier mathematical models based on the balance of C and N assimilated into the biomass (11, 12). Similar concepts are today embedded in most biogeochemical and ecosystem models (13-16), and we will build on such a theoretical basis to derive a general N-release curve.

2 Litter decomposition data

We used litter decomposition data from the LTER Long-term Intersite Fine Litter Decomposition Experiment, LIDET (17-19) and the Canadian Intersite litter Decomposition Experiment, CIDET (20-22). Both experiments are based on long-term reciprocal litterbag studies of decomposition and nutrient mineralization in widely different climatic conditions and using chemically different plant residues. In the present work, data on leaf decomposition for all species with >15 observations were used. Wetland and desert sites, where abiotic nutrient loss pathways are likely to be predominant (23, 24), were excluded. For this analysis, replicate measurements at the same site were averaged, and data points showing a gain of mass or N concentrations higher than five times the initial concentration were considered as outliers. The LIDET litter mass data were converted into C remaining using linear regressions of C

concentrations measured within the same experiment. Observations of N remaining as a function of C lost from LIDET and CIDET experiments are shown in Fig. 1 in the main text.

To make a more comprehensive assessment and to cover a larger range of initial litter N:C we added other datasets to our analysis, including both fine litter and wood decomposition data (denoted by ■), with N:C ratios as low as $r_{L,0} \approx 7 \times 10^{-4}$ (Table S1). We selected datasets with at least two years of both litter mass (or carbon) and nitrogen decomposition of fine litter using the litterbag technique, or based on chronosequence studies in the case of long-term wood decomposition. To have series that were representative of the whole decomposition process, we only considered decomposition datasets with mass loss greater than 40% and >15 data points for any individual litter type (regardless of the site) in the case of fine litter. Lacking detailed temporal measurements of wood decomposition, we also considered several chronosequence studies, even though they provided series of only four to seven data points. Despite their low number, in fact, these points are highly representative, as they generally cover mass losses from zero to more than 70% and integrate both intra- and inter-annual climatic variability. In the chronosequence studies where mass loss data were not reported, we used wood density as a proxy.

Litter mass was converted to C mass using reported C concentrations, or, when no information was available, assuming a C concentration of 50% (mass of C per unit dry weight of litter). Slight errors or temporal changes in this conversion factor (e.g., 25) would not significantly change the N release patterns.

3 Carbon-use efficiency of consumers and aquatic decomposers

Fig. 3A in the main text shows a clear trend of increasing decomposer carbon-use efficiency with increasing initial N content of the litter. This trend is consistent with observations of carbon-use efficiency in decomposers from aquatic environments and consumers at higher trophic levels [Fig. 3B, see also (26)]. In order to compare data from different environments and trophic levels, we considered growth efficiencies only (biomass growth over ingested substrate) and normalized the food source N:C ratios (r_F) by the decomposer or consumer N:C ratio (r_B), using values reported in the literature. We assumed average N:C ratios of 0.23 and 0.18 for marine bacteria (27, 28) and insects (29), respectively. Specific values for terrestrial larvae were reported by Slansky and Feeny (30). Food N concentrations were converted to N:C ratios assuming a C content of 50% in case only the N percentage was given. Since data for aquatic insects only account for the assimilation efficiency (31), the corresponding data points in Fig. 3B (indicated by ×) may overestimate the actual growth efficiency.

4 Model description

In this section we derive an analytical model of the N release curve as a function of remaining C in the litter explicitly based on the mass stoichiometry of the decomposers. Let us denote the total carbon and nitrogen mass contents per litterbag by C_L and N_L , respectively, and their N:C ratio as r_L . Litter carbon is decomposed at a rate D , a fraction e of which is used by decomposers, $G=e \cdot D$, while the fraction $1-e$ is lost through respiration, $R_B=(1-e)D$ (where the parameter e is often called decomposer efficiency,

(16)). Note that, according to the above definition, the respiration R_B accounts for all C losses due to decomposer activity associated with the decomposition flux D , and thus integrate at the annual time scale a variety of short-term respiratory processes (possibly occurring at different trophic levels in the detrital food web) that are not explicitly accounted for. Since our goal is to analyze the patterns of plant litter decomposition across litter types and climatic gradients, we also neglect explicit treatment of microbial succession and other trophic groups, and assume that the decomposer N:C ratio r_B , and the efficiency e are constant in time and representative of the whole decomposer community. As shown later, the specific value of r_B can vary in a wide range without changing the main patterns in the results. This allows us to compute the net mineralization M as the difference between the total nitrogen made available by decomposing litter, $D \cdot N_L / C_L = D \cdot r_L$, and the N needed by the decomposer to assimilate C at a rate G with constant r_B , that is $e \cdot r_B \cdot D$. Accordingly, we obtain

$$M = D(r_L - r_{CR}), \quad (S1)$$

where $r_{CR} = e \cdot r_B$ is the critical N:C ratio. When litter N:C is below the critical value, immobilization is necessary; otherwise net N mineralization occurs (13). The mass balance equations for C_L and N_L in a single litter cohort can thus be written as

$$\frac{dC_L}{dt} = -R_B \quad (S2)$$

$$\frac{dN_L}{dt} = -M = -\frac{R_B}{(1-e)} (r_L - r_{CR}). \quad (S3)$$

Combining Eqs. S2 and S3 yields

$$\frac{dN_L}{dC_L} = \frac{r_L - r_{CR}}{1-e}. \quad (S4)$$

Eq. S4 can be solved in terms of the normalized variables $c = C_L(t)/C_L(0)$ and $n = N_L(t)/N_L(0)$, with the condition $n(c=1) = 1$, leading to the fundamental Eq. 1 describing the N release curve of a single litter cohort as an implicit function of time. Eq. 1 can be also written in normalized form as (Figs. 2 and S1)

$$\xi = \frac{r_L - r_B}{r_{L,0} - r_B} = c^{\frac{e}{1-e}}. \quad (S5)$$

Eq. 1 is equivalent to other formulations derived for a lumped model (11) and in the context of a more complex continuum-quality decomposition model (16). Here it has been derived for a lumped model controlled by a generic decomposition function D , suggesting that the N release curve depends little on the specific choice of model structure and formulation. Notably, Eq. 1 does not depend on the decomposition function D , which typically includes the effects of both N limitation and environmental conditions

on microbial activity (13). Accordingly, even if low availability of inorganic N during the early decomposition phase decreases the rates of litter degradation, it does not alter the basic decomposer stoichiometry. Also, environmental variables such as water availability and temperature affect the C and N temporal dynamics in Eqs. S2 and S3 (17, 22), but not litter stoichiometry evolution (Eq. S4) or the N release curve, as confirmed by experimental evidence (20, 24). This feature allows us to use Eq. 1 to model global N immobilization and release patterns across litter types and climatic conditions.

Fitting Eq. 1 to observations of litter C and N contents provides estimates of the decomposer N:C, r_B , and efficiency, e . However, as already noted by Ågren and Bosatta (16), their product (i.e., r_{CR}) is the primary factor controlling the shape of the N release curves, preventing an independent estimate of r_B and e solely based on Eq. 1. Hence, we assume a constant decomposer N:C, and use Eqs. 1 and S5 to estimate the decomposer efficiency e from least square regression of the observations (Figs. 1, 2, S1). The efficiency e is finally converted to r_{CR} from the definition as $r_{CR}=e \cdot r_B$ (both parameters are shown in Fig. 3A). We tested the sensitivity of the model by choosing $r_B=0.07, 0.1,$ and 0.2 (i.e., decomposer C:N equal to 15, 10, and 5, respectively; see Fig. 3A). The higher and intermediate values of r_B are typical of soil and litter microbial biomass N:C (32-34), while the smaller one is more typical of purely fungal biomass (1, 35). As shown in Fig. 3A, even if we hypothesize a negative trend of r_B from 0.2 to 0.07 with decreasing $r_{L,0}$ (as it would occur from a soil to N-poor plant litter), such variation could not balance the decrease of r_{CR} and thus offset the decrease in efficiency. This proves that such efficiency decrease with $r_{L,0}$ is robust to possible shifts in decomposer composition across litter types.

We used two different regression methods to obtain e : numerical type I nonlinear least square fitting of Eq. 1 using the relative C and N concentrations c and n (as in Fig. 1), and analytical type II regression of the log-transformed normalized form of the N release curve (Eq. S5, Figs. 2 and S1). The values of e estimated from the two methods did not differ significantly; however, the reported estimates of e and r_{CR} are all based on the first regression method.

Supporting Figures and Tables

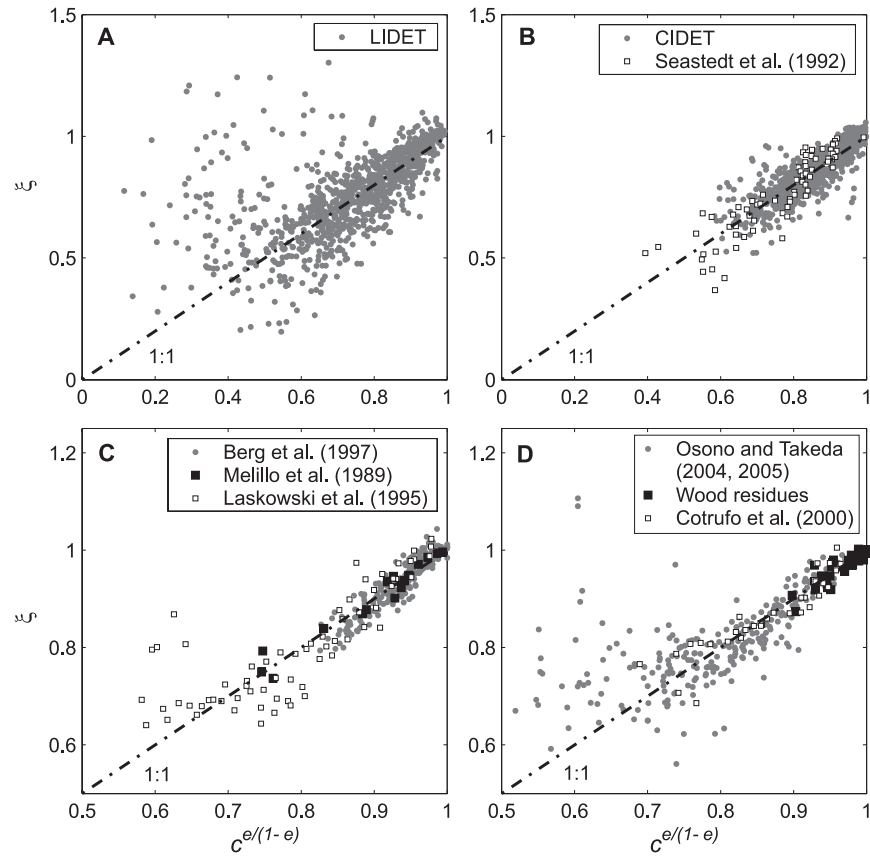


Fig. S1. Plots of the normalized variable ξ (Eq. S5) against $c^{e/(1-e)}$ for each dataset analyzed. As in Fig. 2, the analytical N release curves are fitted to the data with the only free parameter e . Dataset information and correlation statistics of the normalized variables are reported in Table S1.

Tab. S1. Characteristics of the selected datasets.

Dataset reference	Experiment type *	Litter type †	Number of species	Number of data points	$r_{L,0}$ range ($\times 10^{-3}$)	$\frac{C_L(0)}{N_L(0)}$ range	R ‡
Lambert et al. (36)	CS	■	1	7	3.0	332	0.88
Foster and Lang (37)	CS	■	2	12	1.4-1.6	625-714	0.90
Edmonds (38)	LB	■	2	9	4.8-7.2	139-209	0.87
Sollins et al. (39)	CS	■	3	12	1.6-2.2	454-625	0.92
Melillo et al. (40)	LB	▲	1	16	7.1	140	0.98
Seastedt et al. (41)	LB	○	1	71	38.8	25.8	0.89
Means et al. (42)	CS	■	1	5	1.6	620	1.00
Busse (43)	CS	■	1	5	0.7	1327	0.97
Laskowski et al. (44)	LB	□, ▲	2	67	13.7-27.2	36.7-73.2	0.82
Berg et al. (45)	LB	▲	3	211	9.3-11.6	86-107.5	0.93
CIDET (21)	LB	○, □, ▲	10	1076	12.1-25.8	38.8-82.5	0.87
Kankrina et al. (46)	CS	■	3	13	3.4-3.6	277-294	0.94
Cotrufo et al. (47)	LB	□	2	32	18.2-31.3	32-55	0.91
Osono and Takeda (48, 49)	LB	□, ▲	14	260	10.6-58.1	17.2-94.3	0.65
LIDET (18, 19)	LB	○, □, ▲	9	987	8.3-42.4	23.6-120.9	0.60

* LB: litterbag method; CS: chronosequence study.

† ○, grass leaves; □, broadleaved tree and shrub leaves; ▲, conifer needles; ■, woody residues (symbols as in Figs. 2 and 3).

‡ R : Pearson correlation coefficients between ξ and $c^{e/(1-e)}$ for each dataset (Eq. S5, Figs. 2 and 1S); all correlations are highly significant ($P < 0.0001$, except datasets from Lambert (16), $P < 0.01$, and Busse (23) and Edmonds (18), $P < 0.005$).

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